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Modelling dependence of chlorinated hydrocarbons biodegradation on changes of temperature and redox conditions in ATES systems

Modelování závislosti biodegradací chlorovaných uhlovodíků na změně teploty a oxidačně-redukčních podmínkách v ATES systému

DIPLOMOVÁ PRÁCE

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ABSTRAKT

Aquifer Thermal Energy Storage (ATES) je jednou z nejdůležitějších technologií, využívající kolektor k uskladnění energie pro vytápění a ochlazování budov. ATES systém je založen na čerpání studené podzemní vody do budov v průběhu léta, kde je voda ohřívána, a následném injektování ohřáté vody zpět do kolektoru. V průběhu zimy je směr opačný. Teplá voda je čerpána do budov, kde slouží k jejich vytápění a poté je opět injektována do kolektoru.

ATES systém má hlavní vliv na chemické složení podzemní vody díky změnám teploty, mixováním různých oxidačně-redukčních zón a zrychlením proudění podzemní vody v okolí studní ATES systému. Změny teploty a následné změny chemického složení podzemní vody mohou ovlivnit chování kontaminantů. Při instalování ATES systému do kontaminovaného kolektoru, musíme vědět, zdali ATES systém ovlivní chování kontaminace pozitivně nebo negativně.

Tato studie byla prováděna ve spolupráci s nizozemskou firmou Deltares a Utrechtskou Universitou. Cílem práce bylo porozumět vlivu teploty a oxidačně-redukčních podmínek na biodegradaci chlorovaných uhlovodíků. K lepšímu pochopení této problematiky posloužilo sestavení několika modelů v programu SEAWAT. První část byla zaměřena na modelování teplotní závislosti biodegradace chlorovaných uhlovodíků. Modely byly sestaveny pro reakci prvního a nultého řádu s reakčními konstantami, jak nezávislými, tak i závislými na teplotě. Pro ověření jejich správnosti byly dále výstupy z těchto numerických modelů porovnány s analytickým řešením. Druhá část práce je zaměřena na modelování oxidačně-redukčních podmínek, pro které bylo nejprve nutné sestavit bilanční modely v programu PHREEQC. Výstupy z těchto modelů byly následně použity pro modelování vlivu oxidačně-redukčních podmínek na biodegradaci chlorovaných uhlovodíků v programu SEAWAT. Na závěr byl pro zjištění míry šíření tepla v kolektoru sestaven model v programu FEFLOW.

ABSTRACT

The Aquifer Thermal energy Storage (ATES) system is one of the most important techniques, that use the aquifer as an energy storage for heating and cooling the buildings. The operation of the ATES system is based on pumping the cold ground water into the buildings during the summer and then injecting the warmer water back into the aquifer. During the winter, the direction is reversed. Warm water is pumped to the buildings, where it serves for the heating system and then it is injected back into the aquifer.

The ATES system has a main effect on the chemical composition of ground water, because of changes in the temperature of ground water, mixing of water from different redox zone and increasing of ground water flow in the neighbourhood of the wells of the ATES system. The modification in chemical composition and temperature could influence the behaviour of contaminants. If we want to install the ATES system into a contaminated aquifer, we have to know, if the ATES system would influence the behaviour of the contaminant plume positively or negatively.

This study was made to increase the understanding of the dependence between changes of temperature and oxidation-reduction conditions in the ATES system and biodegradation of chlorinated hydrocarbons. In the first part, several scenarios were modelled in the program SEAWAT to show how the temperature influences biodegradation of chlorinated hydrocarbons. The models were set up by using zero order and first order reactions with rate constants dependent and independent on the temperature. A comparative study of numerical and analytical solution was made to verify the correctness of the numerical models. The second part of this project was focused on the dependence between oxidation-reduction conditions and biodegradation of chlorinated hydrocarbons. For the oxidation-reduction conditions was necessary to use the program PHREEQC to balance oxidation-reduction species. The outputs from these models were used in the program SEAWAT for modelling of oxidation-reduction influence on biodegradation of chlorinated hydrocarbons. Furthermore, model in the program FEFLOW was made to determine the heat spreading from the well into the aquifer.

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1 Introduction

This thesis is concerned with application of Aquifer Thermal Energy Storage (ATES) as an environmental-friendly way of heating and cooling of buildings. Nowadays is laid emphasis on taking care about environment, therefore, the utilization of renewable sources have become frequently applied. The ATES systems also belong among renewable sources. However, it is important to solve their affect on quality of ground water aquifer, in which they are situated, preferably before their construction.

During this project, I solved issues of possible contamination of aquifer with ATES system by chlorinated hydrocarbons. My work was focused on numerical models of dependence of biodegradation of chlorinated hydrocarbons on changes in the temperature and oxidation-reduction conditions caused by ATES system.

1.1 Aquifer Thermal Energy Storage

Aquifer Thermal Energy Storage is a special type of underground thermal energy storage (UTES). It was developed in Europe in the 1970‘s and it becomes the most frequently used storage technology. Nowadays it is applied at over 1000 places in The Netherlands, mostly in office buildings (Snijders, 2005).

Ground water thermal energy storage system is very important due to the reduction of the negative impact as a reduction of CO_2, SO_2 and NO_x emission into the atmosphere, which are produced by the traditional energy systems.

This technology uses subsurface water for heating and cooling of the buildings. During the summer, cold water is pumped from the cold well (temperature around 6-9°C) to the buildings (to the ventilation etc.), where is used to their cooling. During the circulation through the building, the water becomes warmer. Then water is injected back into the aquifer through warm well at different place. During the winter, the flow is reversed. The warm water is pumped into the building and it is used for its heating.

The warm water is extracted from the warm well (temperature around 14-17°C) to the heating systems of the building. Then water is injected by cold well back to the aquifer in order to be used during the summer (Figure 1). This cycle repeats seasonally.

This system typically uses water from a minimum depth around 25 meters to maximum depth around 250 meters (Caljé, 2010). At these depths, ground water contaminant is typically present at urban and industrial areas.

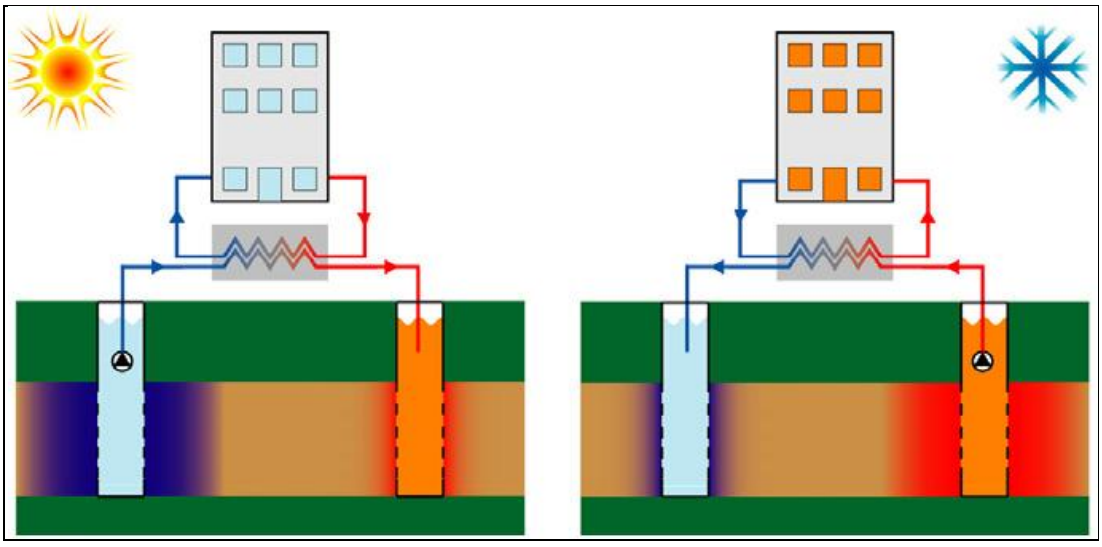

Figure 1: The circulation of ground water in ATES system. During the summer water is pumped from aquifer to the buildings and then injected back into the aquifer (the left side) and during the winter direction is opposite (the right side) (www.iftechnology.nl).

The ATES system affects mainly three factors, which can influence the behaviour of contaminants. The first one is the increased ground water flow in the ATES area. The fast water flow causes fast spreading of contaminants into the clean water. The second one is the change in the temperature around a hot and a cold well. This is important, because the temperature could have positive or negative influence on some contaminants especially organic materials, which can be degraded. The dependence between temperature and degradation is expressed by Arrhenius equation (chapter 1.7). The third factor is mixing of water from different depths of aquifer due to pumping and injecting of water from cold and hot well. The mixing of water from different depth of aquifer could cause changes in oxidation-reduction conditions and it could indirectly

influence the behaviour of contaminants. From these main factors we could indicate, whether the installing of the ATES system would cause potential drawbacks on ground water quality. In addition, the ATES system affects biodegradation rate, solubility, and amount of available organic matter (Ni *et al.*, 2011).

The depth, where ATES systems are installed concurs with the depth of occurrence of chlorinated hydrocarbons. Nowadays one of the most successful remediation technologies of these contaminants is natural attenuation. Natural attenuation is based on natural biodegradation of chlorinated hydrocarbons. Because the temperature and the oxidation-reduction conditions influence biodegradation, ATES system could have an important influence on biodegradation of chlorinated hydrocarbons.

1.2 Natural attenuation

Natural attenuation includes processes, which reduce the concentration of contaminant in soil and ground water. They include a variety of physical, chemical, or biological processes that without human intervention reduce the mass, toxicity, mobility, volume or concentration of contaminates in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants. Natural attenuation occurs at most contaminated sites. However, the right conditions, like temperature, oxidation-reduction conditions and so on, have to exist in ground water to clean location properly and quickly enough (clu-in.org/download/citizens/a_citizens_guide_to_monitored_natural_attenuation.pdf, http://toxics.usgs.gov/definitions/natural_attenuation.html).

1.3 Chlorinated hydrocarbons

Aquifer contamination by organic compounds is widespread environmental problem in Europe and North America. Many of these compounds are biodegradable under aerobic or anaerobic conditions. This degradability is the basis of in situ bioremediation technique for contaminated sites. Numerical model of flow and reactive transport of organic compounds can be helpful tools in designing and monitoring of in situ

bioremediations and in predicting of long-term effects of biodegradation on organic contaminant transport (Schäfer *et al*., 1998).

Chlorinated hydrocarbons are synthetic substances. They have never been in the natural environment; they have always been of human origin. They are one of the most frequent organic contaminants in ground water. Due to their properties, they are often utilized when reducing presence of oils, fats, waxes and resins. These volatile organic substances belong to a group of Dense Non Aqueous Phase Liquids (DNAPL), which are substance in the liquid phase and they react with all the surrounding phases. The main property of DNAPL is that they have a higher density than water. They do not only spread horizontally with ground water flow but they also penetrate through the unsaturated and saturated zone and they occur at the bottom of the collector on the impermeable layer. Due to this property, their removal from ground water is difficult. The main representatives of chlorinated solvents are perchloroethylene (PCE), trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-1,2-DCE) and vinyl chloride (VC).

The main remediation technologies used since the 1970's was pump - and - treat and soil vapour extraction. However, these classical technologies have not been very successful and new remediation technologies, such as monitored natural attenuation, chemical oxidation, and stimulated bioremediation, and permeable reactive barriers, have been tested and used in recent years. Among them, monitored natural attenuation became very popular (Kuchovský and Šráček, 2007). Chlorinated solvents are subjected to the natural attenuation processes like hydrodynamic dispersion, in situ bioremediation, bio venting, surfactants, two – phase extraction and passive barriers (Parker and Mohr, 1996). On most locations, the in situ bioremediation is applied as a less harmful method that uses microorganisms in order to remove or degrade toxic contaminants.

1.4 Biodegradation

Biodegradation (biological decay) is a special case of degradation, which involves chemical decomposition of organic matter (including synthetic) by bacteria or other

biological means. This process contributes to the decrease of quantity of contamination in ground water, because it can potentially transform the components into less toxic.

Chloroethenes can be biodegraded by reductive dechlorination under anaerobic conditions as well as by oxidation under anaerobic and aerobic conditions. The tendency of chloroethenes to undergo reductive dechlorination decreases with a decreasing number of chlorine substituents, whereas with less chlorine substituents chloroethenes more easily undergo oxidative degradation (Tiehm and Schmidt, 2011).

1.4.1 Anaerobic reductive and oxidative degradation

This process uses chloroethenes as an electron acceptor and hydrogen as an electron donor. Ideally, PCE is completely degraded under anaerobic conditions to trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-DCE), vinyl chloride (VC), ethylen (ETH) and methane to carbon dioxide and water (Figure 2) (Fetter, 1999).

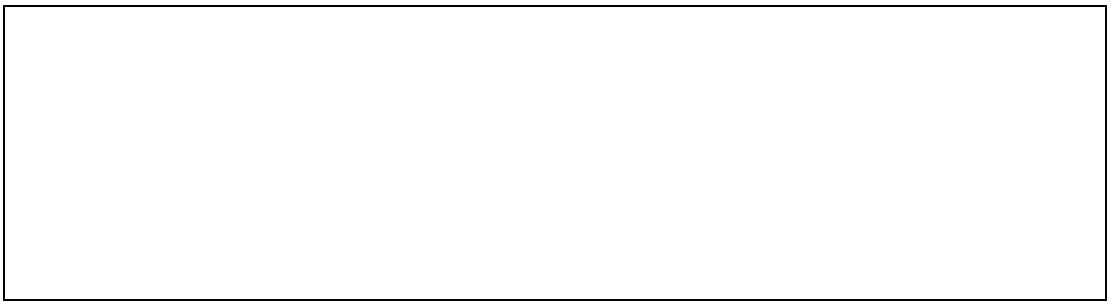

Figure 2: Dechlorination of PCE.

This degradation process is called dehalogenation, or more specifically reductive dechlorination, in which a hydrogen atom biologically replaces a chlorine atom. In this oxidation-reduction reaction, electrons are transferred from the electron donor (H_2) to the electron acceptor (PCE or chlorinated daughter products). Beside the presence of an electron acceptor and donor, nutrients are essential. Other variables that influence growth of bacteria are temperature, pH, acclimation, soil moisture, population density and presence of other bacteria and inhibiting components (Langevoort, 2009).

However, the reductive dechlorination of chlorinated hydrocarbons to non - chlorinated compounds differs according to oxidation-reduction conditions (Kuchovský and Šráček, 2007). The oxidation-reduction conditions in ground water are described in the chapter 1.6.

Anaerobic oxidative biodegradation is only suitable for less chlorinated solvents such as 1,2-DCE and VC, whereas primary contaminants (as are PCE and TCE) do not undergo oxidative biodegradation (Kuchovský and Šráček, 2007).

1.4.2 Aerobic oxidative degradation

Anaerobic oxidation has been described only in laboratory studies and it is not known really well. Under anoxic conditions, chloroethenes can be oxidized both cometabolically and metabolically. During cometabolic degradation, the chloroethenes are only degraded fortuitously. The degrading enzymes are actually produced for the degradation of bacterial growth substrates like methane, ethane, ammonium or aromatic pollutants (Tiehm and Schmidt, 2011).

1.5 Bioremediation

Bioremediation is type of biodegradation and includes all natural processes, which are implemented by microorganisms like bacteria. Microorganisms are substances, which leads to the destruction of some organic molecules. The bioremediation is based on acceleration of these natural biodegradation processes or on targeted biodegradation. Processes of bioremediation reduce risks of undesirable substances and the risks of persistence of unknown transformation products in environment. Bioremediation is therefore biodegradation method that leads to the cleaning of contaminated environment. There are two methods of bioremediation, fertilization and seeding, that differ in the conditions of environment, presence and type of microbes and character of pollution (Horáková, 2006)

Fertilization, also known as nutrient enrichment, is the method of adding nutrients such as phosphorous and nitrogen to a contaminated environment to stimulate the growth of

microorganism capable of biodegradation. Limited supplies of these nutrients in nature usually control the growth of native microorganism populations. When more nutrients are added, the native microorganism population can grow rapidly, potentially increases the rate of biodegradation (www.epa.gov/osweroe1/content/learning/bioagnts.htm).

Seeding is the addition of microorganisms to the existing native population in contaminated environment. As with fertilization, the purpose of seeding is to increase the population of microorganisms, that could contribute to the biodegradation of contaminants (http://www.epa.gov/osweroe1/content/learning/bioagnts.htm).

1.6 Rate equations

The rate law is a mathematical expression of the reaction kinetic. The kinetic of degradation of chlorinated hydrocarbons is mostly described by zero order or first order reactions. The degradation of chlorinated hydrocarbons was modelled for both of them. They differ with the type of limitation factors. The zero order reaction rates are limited by the slow release of electron donor from the sediment (Zuurbier *et al.*, 2011; McCarty, 1997). The first order reaction rates depend on the contaminant concentration (Suarez and Rifai, 1999).

1.6.1 Zero - order reactions

A zero – order reaction has a rate independent on the concentration of the reactant (s). Increasing or decreasing the concentration of the reacting species, will not speed up or slow down the rate of the reaction and the reaction rate is equal to the rate constant. Zero – order reactions are typically found when a catalyst, surface, or other material required for the reaction is saturated by the reactants in this reaction.

The rate law for a zero - order reaction is (Merkel and Planer-Friedrich, 2008):

$$r = k \tag{1}$$

where:

- r is reaction rate and
- k is reaction rate coefficient, or rate constant of chemical reaction (concentration/time).

It can be shown by solving the mass balance equation for the system that it holds:

$$r = -\frac{d[A]}{dt} = k \tag{2}$$

where t is time and A is concentration of the particular chemical, see (Merkel and Planer-Friedrich, 2008).

If this differential equation is integrated, it gives an equation, which is often called Integrated zero – order rate law. This law shows how fast or slow the degradation goes and it is specific for each component, because of different rate constants. It is a relationship between the concentration of reactant and time, so the concentration of reactant is expressed as function of time (Merkel and Planer-Friedrich, 2008):

$$(A) = -kt + (A_0) \tag{3}$$

where:

- A is the concentration of the chemical of interest at a time t,
- A_0 is the initial concentration at a time t = 0 and
- k is zero order reaction rate constant, or rate constant of chemical reaction (concentration/time).

1.6.2 First - order reactions

The rate of first order reactions depends on the concentration of only one reactant. Other reactants can be present but each one will be zero – order. The rate law for a simple first order irreversible reaction like (Fitts, 2002)

$$A \rightarrow products \tag{4}$$

with respect to a reactant A is (Fitts, 2002):

$$r = \frac{d(A)}{dt} = -k(A) \tag{5}$$

where:

r	is the first order rate,
k	is the first order reaction rate constant [1/s],
(A)	is the concentration of the species A and
t	is the time [s]

The integrated first – order rate law is (Fitts, 2002):

$$(A) = (A_0) \cdot e^{-kt} \tag{6}$$

where:

(A)	is the concentration of the chemical of interest at time t,
(A_0)	is the concentration at a time t = 0,
k	is the first order reaction rate constant [1/s] and
t	is the time [s].

1.6.3 The relationship between zero and first order rate constants

Zero and first order rate equations are balanced to give the same rate at a given reference concentration. The dependence between zero and first order rate constant is expressed by following equation:

$$k_0 = k_1 \cdot m \tag{7}$$

where:

k_0 is zero order reaction rate constant,

k_1 is first order reaction rate constant and

m is referential concentration of each species.

1.7 Arrhenius equation

The dependence between temperature and reaction constant is expressed by Arrhenius equation.

$$k = A \cdot e^{-E_a / R \cdot T} \tag{8}$$

where:

A is pre - exponential factor – constant,

k is rate constant of chemical reaction,

E_a is activation energy,

R is universal gas constant ($R = 8.314 * 10^{-3}$ kJ mol^{-1} K^{-1}) and

T is temperature.

Rate constant from Arrhenius equation can be used to compute the temperature coefficient Q_{10}. The temperature coefficient is measured from the rate of change in biological or chemical system as a consequence of increasing temperature by 10°C. This temperature coefficient could be calculated from the equation 9 (page 20) (Xiao, 2000):

$$Q_{10} = \left(\frac{k_1}{k_2} \right)^{10/(T_1 - T_2)} \quad (9)$$

where:

Q_{10} is the temperature coefficient and

k_1, k_2 are the rate constants of chemical process at temperatures T_1, T_2.

For zero order reaction the rate constants are normally replaced by their corresponding rates r_1 and r_2.

1.8 Oxidation-reduction conditions in ground water contaminant plumes

Evaluation of the oxidation-reduction conditions in contaminated ground water by chloroethenes is very important for understanding the behaviour of the pollution in the plume and for selecting a remediation approach. (Christensen *et al.*, 1999).
The microbial mediated oxidation-reduction reactions are the most important biochemical processes of pollutants in ground water. Microorganisms can degrade an organic pollutant through different types of terminal electron acceptor processes such as aerobic respiration, denitrification, Mn (IV) reduction, Fe (III) reduction, sulphate reduction and methanogenesis (Rolle *et al*., 2008).

During reductive dechlorination, hydrogen acts as the electron donor and halogenated compounds, such as chlorinated solvents, act as electron acceptor and thus become reduced, as shown in the following half reaction (Aziz and Newell, 2000):

$$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^- \quad (10)$$

Oxidation-reduction conditions and their corresponding chemical equations are in Table 1 (page 21) (Lensing *et al.*, 1994).

Table 1: Redox reactions in aquifer contaminated by organic components.

Aerobic respiration $CH_2O + O_2 \rightarrow CO_2 + H_2O$
Denitrification $CH_2O + 4/5\ NO_3^- + 4/5\ H^+ \rightarrow CO_2 + 2/5\ N_2 + 7/5\ H_2O$
Mn (IV) - reduction $CH_2O + 2\ MnO_2 + 4\ H^+ \rightarrow CO_2 + 2\ Mn^{2+} + 3\ H_2O$
Fe (III) – reduction $CH_2O + 4\ Fe(OH)_3 + 8\ H^+ \rightarrow CO_2 + 4\ Fe^{2+} + 11\ H_2O$
Sulphate – reduction $CH_2O + 1/2\ SO_4^{2-} + 1/2\ H^+ \rightarrow CO_2 + 1/2\ HS^- + H_2O$
Methanogenesis $CH_2O \rightarrow 1/2\ CO_2 + 1/2\ CH_4$

For chloroethene contaminants, the tendency to undergo reductive dechlorination decreases with decreasing number of chlorine substituents. PCE, with its four chlorine atoms, is a better oxidant than other naturally occurring electron – accepting species in ground water system. PCE readily undergoes reductive dechlorination to TCE except in aerobic aquifers. Reductive dechlorination of TCE and DCE occurs under Fe (III) conditions and in more strongly reducing environments. Reductive dechlorination of DCE to yield VC apparently requires at least sulphate - reducing conditions, but readily in methanogenic environments. VC is the least oxidized chloroethene. Therefore reductive dechlorination of VC to the non – chlorinated product, ethane, is slow and significant only under highly reducing, methanogenic conditions (Bradley, 2000; Vogel *et al.*, 1987; Vogel and McCarty, 1985).

With decreasing number of chlorine substituents, the reductive potential decreases too and consequently, the reductive dechlorination of chloroethene contaminant is often incomplete in groundwater system and frequently leads to the accumulation of DCE and VC (Bradley, 2000).

The oxidation-reduction conditions determine the oxidation-reduction potential (Kravonen, 2002). The oxidation-reduction potential of ground water (*Eh*) is a measurement of electron activity that indicates the relative tendency of a solution to accept or transfer electrons. The oxidation-reduction potential of ground water generally ranges from -400 to 800 mV. Oxidation-reduction potential can be used to provide real

time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Oxidation-reduction reactions in ground water are usually biologically mediated and therefore, the oxidation-reduction potential of a ground water system influences rates of the biodegradation. Knowledge of the oxidation-reduction potential of ground water is also important because some biological processes only operate within a prescribed range of oxidation-reduction conditions. Therefore, the oxidation-reduction potential of ground water can be used as an indicator of certain geochemical activities such as sulphate reduction (Kravonen, 2002).

1.9 Heat transport in ground water

In ATES system, it is very important to most accurately know the behaviour of aquifer, which could be affected by changes in water flow, contaminant transport and temperatures around the injection and pumping wells.

The injection of hot water into a ground water storage system will have a pronounced effect on the specific storage and mass flow within the aquifer. These effects will result from differences in viscosity, density, specific heat, and thermal conductivity between injected water and the natural ground water (Reed and Reddell, 1980).

Physical processes affecting heat transport within a storage aquifer, similarly to transport of chemical compounds, include advection, dispersion and diffusion. The diffusion of heat depends on the thermal conductivity and heat capacity of the aquifer. The fluid phase as well the solid phase plays important role in heat transport in aquifer and ultimately control the recovery efficiency of storage energy (Dincer and Rosen, 2010).

Considering the equality (thermal equilibrium) of the temperature between the fluid and the rock matrix and assuming that convection is mainly governed by the pressure gradient, the balance equation of heat transfer in a saturated porous medium in transient conditions can be written as equation 11 on the page 23 (Fossoul *et al.*, 2010).

$$\left(\frac{\rho_m c_m}{n_e \rho_w c_w}\right) n_e \frac{\partial T}{\partial t} = \overrightarrow{div}\left[n_e \left(\frac{\lambda_m}{n_e \rho_w c_w} + D\right) \overrightarrow{grad} T \right] - \overrightarrow{div}\left(n_e \vec{v}_e T\right) + \frac{q'}{\rho_w c_w} \qquad (11)$$

Where:

T is the temperature of the fluid in the porous medium is the main variable,

ρ_m is the volumic mass of the saturated porous medium,

c_m is the specific heat capacity of the saturated porous medium,

n_e is the effective porosity of the medium,

ρ_w is the volumic mass of water,

c_w is the specific heat capacity of water,

λ_m is the thermal conductivity of the porous medium,

D is the tensor of thermo-mechanical dispersion,

v_e is the effective velocity of ground water (function of the hydraulic conductivity and the inverse of effective porosity) and

q' is the source/sink term.

The first term describes changes of the heat stored in a balance volume due to the temperature changes with time. The second term represents the conductive/dispersive portion of the transport, the third term of the differential equation characterizes the heat transport by convection, and the fourth term represents heat sources (Pelka, 1983).

1.10 Modelling methodology

The numerical models were created in order to find out how changes in temperature and in oxidation-reduction conditions within the aquifer with ATES system influence biodegradation and how is temperature distributed in the surrounding of the wells. I used program MODFLOW for simulation of transport processes. Reactive transport of contaminant (including biodegradation) was modelled in modified version of program SEAWAT. For my studies, the program PHT3D was sufficient to use, because SEAWAT is a program for modelling of flow and transport with density or viscosity dependence and that was not included in my project. I used the SEAWAT, because I worked with data and results obtained from K. G. Zuurbier, who used modified version

of the SEAWAT. In his model, SEAWAT was used to simulate the Multi Node Well and effects of density and viscosity changes due to the temperature differences in the ATES system in ground water flow. The oxidation-reduction conditions were modelled using geochemical model PHREEQC. After those calculations, the outputs were used into the SEAWAT models to solve connection between oxidation-reduction conditions and biodegradation of chlorinated hydrocarbons. Eventually, the model of heat transport was set up in program FEFLOW in order to evaluate the temperature distribution and heat balance in the wells surrounding.

1.10.1 MODFLOW

Modflow is a program for numerical solving of the three-dimensional (3D) ground water flow equation for a porous medium. The program is based on the finite difference method (Harbough *et al.*, 2000).

The partial differential equation for the 3D flow of ground – water that is used in MODFLOW is following (Harbough *et al.*, 2000):

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)+w=S_S\frac{\partial h}{\partial t} \qquad (12)$$

where:

K_{xx}, K_{yy}, K_{zz}	are values of hydraulic conductivity along the x, y, z coordinate axes [m/s],
h	is the hydraulic head [m],
w	is density of sources, i.e. volume of water that arises in unit volume of the porous medium per unit time [s^{-1}],,
S_s	is the specific storage of the porous material [m^{-1}] and
t	is time [s].

1.10.2 PHT3D

PHT3D is model for modelling 3D reactive multicomponent transport in saturated porous media. It consists of the model of chemical reaction PHREEQC (geochemical code for the quantification of reaction) coupled with the model of transport MT3DMS (program for simulation of 3D advective-dispersive multi species transport). PHT3D program is usually used for modelling biochemical processes, for example (Prommer and Post, 2010):

- aqueous complexation,
- oxidation-reduction reactions,
- mineral precipitation / dissolution,
- ion exchange reactions,
- growth and decay of bacterial groups,
- dissolution from a multi component NAPL mixture (PHT3D Tutorial).

PHT3D simulation is built on the base of groundwater flow field obtained in advance by modelling of separate flow mostly using the program MODFLOW.

The partial differential equation describing the reactive transport of contaminant of species *k* in 3D transient ground water flow systems is following (Zheng and Wang, 1999):

$$\frac{\partial\left(\theta C^{k}\right)}{\partial t}=\frac{\partial}{\partial x_{i}}\left(\theta D_{ij}\frac{\partial C^{k}}{\partial x_{j}}\right)-\frac{\partial}{\partial x_{i}}\left(\theta v_{i}C^{k}\right)+q_{S}C_{S}^{k}+\sum R_{n} \qquad (13)$$

where:

C^k is the dissolved concentration of species *k*, [kg·m^{-3}],

θ is the porosity of the subsurface medium, [-],

t is the time, [s],

x_i is the distance along the respective Cartesian coordinates axis, [m],

D_{ij} is the hydrodynamic dispersion coefficient tensor, [m^2·s^{-1}],

v_i is the average pore-water velocity, [$m \cdot s^{-1}$]; satisfying the relation $v_i = w_i / \theta$ where w is volumetric flux density,

q_s is the source density, i.e. volume of the phase arising per unit time and unit volume of aquifer [s^{-1}],

C_s^k concentration of the species k, in the source q [$kg \cdot m^{-3}$],

$\sum R_n$ is the chemical reaction term, [$kg \cdot m^{-3} \cdot s^{-1}$].

1.10.3 SEAWAT

SEAWAT is the program developed to simulate 3D, variable densities, transient ground water flow in porous media. The source code for SEAWAT was developed by combining MODFLOW and MT3DMS into a single program that solves the coupled flow and solute transport equations (Guo and Langevin, 2002).

Although SEAWAT is not explicitly designed to simulate heat transport, temperature can be simulated as one of the species by entering appropriate transport coefficients. Heat conditions can be represented in SEAWAT by assigning a thermal diffusivity for the temperature species, instead of a molecular diffusion coefficient for a solute species. (Langevin *et al.*, 2008).

In this project a modified version of SEAWAT, that includes the Multiple Node Well. The Multi Node Well is used to simulate the distribution of injected and recovered water over the multiple filtered intervals of the wells and mixing of different types of water in from several depth of aquifer (Halford and Hanson, 2002).

1.10.4 PHREEQC

PHREEQC is a computer program designed to perform a wide variety of chemical reactions and transport processes in natural or polluted water (Parkhurst and Appelo, 1999). The geochemical model PHREEQC is capable of simulating a wide range of equilibrium reactions between water and mineral, ion exchangers, surface complexes, solid solutions, and gases. It also has a general kinetic formulation with rate equations that allows modelling of non – equilibrium mineral dissolution and precipitation, microbial reactions, decomposition of organic compounds, and other kinetic reactions

(Charleton and Parhurst, 2011). Kinetic and equilibrium reactions can be interconnected, for example by linking the number of surface site to the amount of a kinetic reaction that is consumed (or produced) during the course of model period. The possibility to extend chemical database allows involvement of almost any chemical reaction that is recognized to influence rain-, soil-, ground- and surface water quality. PHREEQC is program capable of simulating a variety of geochemical reactions for a system including for example:

- mixing of waters,
- addition of net irreversible reactions solution,
- dissolving and precipitation phases to achieve equilibrium with the aqueous phase,
- effect of changing temperature,
- ion - exchange equilibrium,
- surface – complexation equilibrium,
- fixed – pressure gas – phase equilibrium,
- advection transport, and diffusion or dispersion in 1D transport
- kinetic controlled reactions,
- solid solution and fixed volume gas - phase equilibrium.

PHREEQC complete accounting for elements in solid, aqueous and gas phase, molalities and activities of aqueous species, mole balance of hydrogen and oxygen to account mass of water in the aqueous phase, *pH*, *Eh*, saturation indices, mole transfers of phases to achieve equilibrium and so on (Parkhurst and Appelo, 1999).

1.10.5 FEFLOW

FEFLOW is an interactive finite – element simulation system for subsurface flow and transport modelling with an extensive list of functionalities, including 2D and 3D variably saturated transient or steady state flow, variable fluid density mass, heat transport and reactive multi - species transport (Trefry and Muffels, 2007).

FEFLOW can be efficiently used to describe the spatial and temporal distribution and reactions of ground water contaminant, to geothermal processes, to estimate the duration and travel times of chemical species in aquifer, to plan and design remediation strategies and interception techniques, and to assist in designing alternatives and effective monitoring schemes (DHI – WASY Software, 2012).

FEFLOW was used in this project to model heat transport, which is expressed by Fourierian heat flux (Diersch, 2009).

2 Modelling

The first part of this project is focused on the numerical models of the ATES system in the program SEAWAT and its effect on biodegradation of chlorinated hydrocarbons. Several scenarios were set with different input data. The results were compared within each other in order to show their importance and reliability. In the first instance, I started with basic models with and without the ATES system in versions with zero and first order reactions. Goals of these models were to investigate how the changes in temperature, caused by ATES system, are important for biodegradation of chlorinated hydrocarbons. These models were also used to compare differences between first and zero order reactions. For more effective evaluation of temperature influence on biodegradation I set the difference between the temperature of the cold and hot well besides the values of ATES system to the higher values. Furthermore, models with different activation energy were made, because it is one of the members in Arrhenius equation and therefore it is important for reaction rate.

The second part of the project was focused on the modelling of mixing several types of oxidation-reduction zones, due to the pumping and injecting of water, and the influence of this process on biodegradation of chlorinated hydrocarbons. Oxidation-reduction zones were modelled in geochemical program PREEQC. The output concentrations of each species from these models were used in the basic model of biodegradation in the program SEAWAT to model the development of oxidation-reduction conditions in aquifer at time. Based on the previous results I tried to model the relation between mixed oxidation-reduction zones and biodegradation of chlorinated hydrocarbons through oxidation-reduction potential.

In the last section a model of heat transport was built in the program FEFLOW, to show the direction of heat spreading from the ATES wells within the aquifer.

2.1 Primary model of contaminant transport and biodegradation (Koen Gerardus Zuurbier)

For the modelling of the dependence between temperature and oxidation-reduction conditions and biodegradation, I used numerical model made by Koen Gerardus Zuurbier who used the model for his studies of the existing ATES system at Uithof. In this chapter, I briefly describe the Scenario 2 (Zuurbier *et al.*, 2013), which I used for my modelling.

At the location Uithof the subsurface consist of sand and gravel aquifers and of low permeable clay aquitards. In numerical model, the subsurface was divided into 11 layers according to different hydraulic conductivity (Table 2). ATES wells are installed into the layer 3, 6, 7, 8 and 9. The cold well is in the western part and the hot well is in the eastern part of the modelled domain.

Table 2: Layers and corresponding hydraulic conductivities.

Layer	Thickness (m)	Horizontal hydraulic Conductivity (m/d)	Vertical hydraulic Conductivity (m/d)
1	4.8	0.1	0.1
2	13.2	31	15.5
3	15	31	15.5
4	8	25	12.5
5	2	0.25	0.025
6	8.09	35	17.5
7	0.3	35	17.5
8	0.3	35	17.5
9	0.3	35	17.5
10	6	0.5	0.005
11	76	10	5

The main properties of this aquifer are transmissivity of 1320 m^2/d, hydraulic resistance of 280 d (underlying aquitard has a hydraulic resistance 1200 d), hydraulic gradient of 0.00024 m/m, porosity of 0.35 and hydraulic conductivity stated in Table 2. From these values the volumetric flux density was estimated as 7 m/yr in south – west direction. The total volume 147.951 m^3 of water was pumped from the warm well to the cold well during winter and the total volume 132.232 m^3 of water was pumped from the cold well

to the hot well during the summer. The temperature of the warm water was set to 16°C, the temperature of the cold well on the value 8°C and the initial temperature in the aquifer as a 10.5°C. The pumping regime of cold and warm well is shown in Table 3, each stress period corresponds to 7 or 8 days.

Table 3: The pumping regime of cold and warm well.

Well	Stress periods
Cold	1 – 18
Warm	19 – 53
Cold	54 – 70
Warm	71 – 105
Cold	106 – 123
Warm	124 – 158
Cold	159 – 176
Warm	177 - 211

The total extend of the model domain was 1760 m in the west-east direction and 1323 m in the north-south direction and the minimal distance between each well and the nearest edge was 800 m.

The ATES system at Uithof was used to combine the existing ATES system with the fictive contamination of chlorinated hydrocarbons to model the influence of the ATES system on the contaminant behaviour. The concentration of PCE as a source of contamination was situated close to the hot well at the base of the lower aquifer.

Values of the characteristics utilized in the groundwater flow and solute transport model are presented in Table 4 (page 32).

The sediment limited zero order reactions were used for the situations, where biodegradation is independent on the contaminant concentrations and the degradations is limited by slow release of electron donor from sediment. The contaminant limited first order reactions were used for situations, where sufficient organic material is dissolved and thus the reaction rates depend on the concentration of contaminant.

Table 4: Input data for numerical model.

Parameters	**Value**	**Unit**
Model dimensions $l_x \times l_y, \times l_z$	1760×1323×135	m×m×m
Discretisation Δx	3-120	m
Discretisation Δy	0.5-80	m
Discretisation Δz	0.3-79	m
Horizontal Hydraulic Conductivity K_h	0.1-35	$m \cdot d^{-1}$
Vertical Hydraulic Conductivity K_v	0.01-17.5	$m \cdot d^{-1}$
Effective Porosity η	0.35	-
Specific Yield	0.25	-
Specific Storage	0.0001	m^{-1}
Longitudinal Dispersivity a_t	1	m
Horizontal Transversal Dispersivity a_T *(h)*	0.1	m
Vertical Transversal Dispersivity a_T *(v)*	0.01	m
Molecular Diffusion coefficient D_m (PCE / TCE / DCE / VC)	3.76 / 4.06 / 4.32 / 5.79 · 10^{-5}	$m^2 \cdot d^{-1}$
Distribution Coefficient K'_d (PCE / TCE / DCE / VC)	1.26 / 0.32 / 0.24 / 0.01 · 10^{-3}	$m^3 \cdot kg^{-1}$
Bulk density ρ (clay / sandy clay / sand)	1430 / 1573 / 1716	$kg \cdot m^{-3}$
Sediment limited zero – order rate constant (PCE / TCE / DCE / VC) 10^{-4}	1.86 / 1.74 / 1.86 / 0.11	$mg\ L^{-1}d^{-1}$
Contaminant limited first – order rate constant (PCE / TCE / DCE / VC) 10^{-3}	0.5 / 0.5 / 0.25 / 0.125	d^{-1}

2.2 Dependences of reaction rate constants on the temperature

Several scenarios were modelled for the first and zero order reaction to compare the sediment and contaminant limited biodegradation and their dependence on the temperature. To solve the relation between temperature and biodegradation it was necessary to deduce the relationship between the reaction rate constant and temperature.

2.2.1 First order reaction rate constants of PCE and TCE depending on the temperature

For modelling of dependence between temperature of ATES system and biodegradation, we had to find the relationship between reaction rate constants and temperature. Due to a lot of unknowns as an activation energy and pre-exponential factor, it was not possible to use Arrhenius equation. I had to use values of the first order reaction rate constants of

PCE and TCE for different temperature from literature (Schaerlaekens *et al.*, 1999). Making use of these values, I generated an exponential function giving the reaction rate constants of PCE (Figure 3) and TCE (Figure 4, page 34) as a function of temperature. For other species as a DCE and VC there were not enough values of reaction rates to get a reasonable equations and I had to use constant values of reaction rate constant for them. Therefore, the dependence of biodegradation on temperature was modelled only for PCE and TCE.

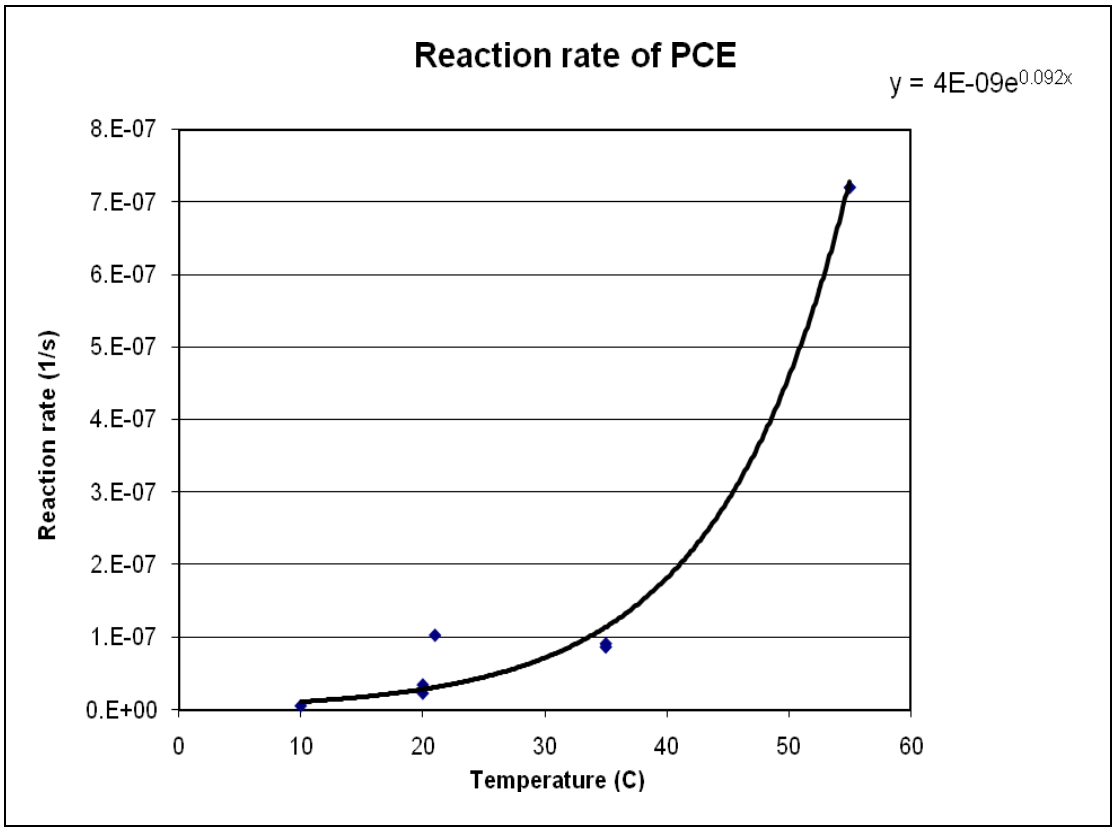

Figure 3: Dependence of reaction rate constant of PCE on the temperature.

If we use equation 9 (page 20) for exponential function of rate coefficient and values from Figure 3 we get the temperature coefficient of PCE Q_{10} = 2.52. It is valid for the whole range of temperature from 10 to 55°C.

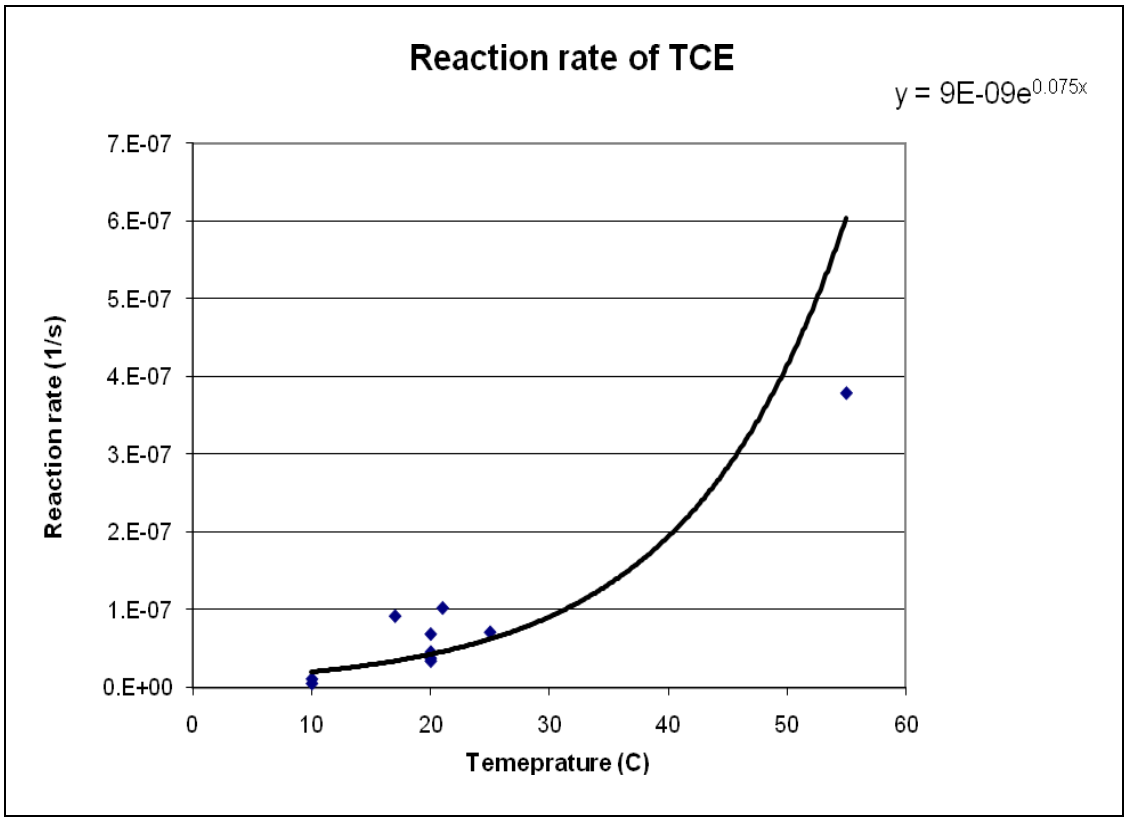

Figure 4: Dependence of reaction rate constant of TCE on the temperature.

Using equation 9 (page 20) for exponential function of rate coefficient and values from Figure 4 we get the temperature coefficient of TCE Q_{10} = 2.13. As for PCE the coefficient is valid for the whole range of temperature from 10 to 55°C.

2.2.2 Zero order reaction rate constants of PCE and TCE depending on the temperature

For zero order reaction not enough values were found in the literature to develop the relationship between zero order reaction rate constant and temperature as for first order reaction. To get the equation for zero order reaction rate constant and temperature equation 7 (page 19) was used with reference concentration and reaction rate constant of first order reaction. The reference concentration is equal to initial concentration of PCE ($1 \cdot 10^{-6}$ g/l). The initial degradation rates for zero and first order reactions are equal for this concentration. For all species, the same value of reference concentration was used (equation 14, page 35).

$$c\,(\mathrm{PCE}) = c\,(\mathrm{TCE}) = c\,(\mathrm{DCE}) = c\,(\mathrm{VC}) = 0.000001\ \mathrm{g/l} \quad (14)$$

2.3 Numerical modelling of biodegradation of chlorinated hydrocarbons depending on temperature of ATES system

Several versions of scenario 2 (Zuurbier *et al.*, 2013) were created to understand how temperature influence the biodegradation. All models were set up for the first order and zero order reaction rate constants.
The models were run in the program SEAWAT. For modelling of the dependence between temperature in the ATES system and biodegradation of chlorinated solvents it was sufficient to use the program PHT3D. However, the model by K. G. Zuurbier, which I used as a default model for my scenarios, was set in the SEAWAT, because K. G. Zuurbier used the Multiple Node Well, density and viscosity changes, which are not available in the PHT3D.

Some scenarios were run for 50 stress periods (approx. 1 year) and some for 1000 stress periods (approx. 19 years). The difference was made because models with 1000 stress periods run much longer than with 50 stress periods. For some type of scenarios it was not necessary to make a model with 1000 stress periods and it was sufficient to run it only in shortened versions with 50 stress periods.

2.3.1 Models with first and zero order reactions

Firstly, I set the models for first and zero order reactions. I started with models for just 50 stress periods, which respond to 351 days. In these versions were tested settings of the model, especially the equations for reaction rate constant and their dependents on temperatures.

The dependence of the PCE first order reaction rate constant on temperature results from Figure 3 (page 33) and corresponds to the equation 15 (page 36).

$$k^{PCE} = 4 \cdot 10^{-9} \cdot e^{(0.0926 \cdot T)} \quad (15)$$

where:

k^{PCE} is the first order reaction rate constant of PCE and

T is the temperature.

The dependence of TCE first order rate constant on the temperature we can see in Figure 4 (page 34) and the equation is:

$$k^{TCE} = 9 \cdot 10^{-9} \cdot e^{(0.0759 \cdot T)} \quad (16)$$

where:

k^{TCE} is the first order reaction rate constant of TCE and

T is the temperature.

For the zero order rate constants, I used edited equation for first order rate constant, which were only multiplied by referential concentration of species according to equation 7 (page 19). The value 10^{-6} g/l was used as a referential concentration (chapter 2.2.2).

The equation of zero order reaction rate constant of PCE is:

$$k_0^{PCE} = 10^{-6} \cdot 4 \cdot 10^{-9} \cdot e^{\left(0.0926 \cdot T\right)} \quad (17)$$

where:

k_0^{PCE} is the zero order reaction rate constant of PCE and

T is the temperature.

The zero order reaction rate constant of TCE is given by the equation 18:

$$k_0^{TCE} = 10^{-6} \cdot 9 \cdot 10^{-9} \cdot e^{(0.0759 \cdot T)} \qquad (18)$$

where:

k_0^{TCE} is the zero order reaction rate constant of TCE and

T is the temperature.

These equations of reaction rate constant, first order as well as zero order, were put into the database file. The values of reaction rate constants were also modified in PHT3D input file.

In Table 5 and 6 there is presented the summarization of the first and zero order rate constants of PCE and TCE used for the models with and without dependence on the temperature. The reference temperature, which was used for the models without temperature dependence, was set to the value 10.5°C.

Table 5: Rate constants of PCE for first and zero order reactions.

	1.order rate constant – k_1	0.order rate constant – k_0
PCE (T_{ref} =10.5°C)	$4 \cdot 10^{-9} \cdot e^{(0.0926 \cdot 10.5)} = 1.058 \cdot 10^{-8}$	$k_1(10.5) \cdot 10^{-6} = 1.058 \cdot 10^{-14}$
PCE (T)	$4 \cdot 10^{-9} \cdot e^{(0.0926 \cdot T)}$	$k_1(T) \cdot 10^{-6} = 4 \cdot 10^{-15} \cdot e^{(0.926 \cdot T)}$

Table 6: Rate constants of PCE for first and zero order reactions.

	1.order rate constant – k_1	0.order rate constant – k_0
TCE (T_{ref} =10.5°C)	$9 \cdot 10^{-9} \cdot e^{(0.0759 \cdot 10.5)} = 1.997 \cdot 10^{-8}$	$k_1(10.5) \cdot 10^{-6} = 1.997 \cdot 10^{-14}$
TCE (T)	$9 \cdot 10^{-9} \cdot e^{(0.0759 \cdot T)}$	$k_1(T) \cdot 10^{-6} = 9 \cdot 10^{-15} \cdot e^{(0.0759 \cdot T)}$

All these equations and values were used in the program SEAWAT to model temperature dependence on biodegradation of chlorinated hydrocarbons.

2.3.2 Scenarios with and without ATES system

In the second part, I created models with and without ATES system to know how the ATES system can affect the biodegradation. The models were run with all 988 stress periods, each has 7 or 8 steps equal to the number of days, which corresponded to the total 7020 days. The models were set with first and zero order reactions, with and without temperature dependence. For the reaction rate constants the same equations were used as in the previous chapter Table 5 and 6 (page 37).

Scenarios, which were made to compare biodegradation of chlorinated hydrocarbons with and without ATES system and with and without temperature dependence, are summarized below:

- **Model without ATES system**: for comparison, I made also model without ATES wells, which would affect the temperature in the aquifer. Temperature has a constant value 10.5°C in the whole modelled area and it is constant during the whole time. In this version, only the biodegradation was modelled as a first order and as a zero order reaction without temperature dependence.

- **Model with ATES system without dependence between biodegradation and temperature**: this version corresponds to the Zuurbier's scenario 2 (Zuurbier *et al.*, 2013) without any changes. This model was run again for both reaction rate constant (first and zero order). The temperature of the cold well was set to 8°C and the temperature of the hot well to 16°C, reference temperature was again 10.5°C. In this case, the changes in the temperature of the aquifer do not affect the biodegradation.

- **Model with ATES system with biodegradation dependence on the temperature**: in this version, I included the equations for the dependence between reaction rate constant (first order and zero order) of PCE and TCE and the temperature. The reaction rate constant of PCE and TCE are changing with temperature according to the equations 15 – 18 (page 36 and 37).

2.3.3 Models with bigger differences in the temperatures of cold and hot well

The models with bigger differences in the temperature were run to determine the extent of influence of the temperature on the biodegradation. I tested sensitivity of the results to the changes of the temperature. These models were run only for 50 stress periods (1 year) for first and zero order reaction rate constants in the versions with and without dependence of biodegradation on the temperature:

- **Models, in which the temperature of the cold well is 3°C and the temperature of the hot well is 25°C.**

- **Models, where the temperature of the cold well is 5°C and the temperature of the hot well is 80°C.**

For the models with bigger differences in the temperature 8 versions were run, 4 for each part:

- the models with first order reaction rate constants, which are independent on the temperature,
- the models with first order reaction rate constants, which are dependent on the temperature,
- the models with zero order reaction rate constants, which are independent on the temperature and
- the models whit zero order reaction rate constants, which are dependent on the temperature.

2.3.4 Models with different values of activation energy

The reaction rate constants depend also on the activation energy, which is determined by the Arrhenius equation (equation 8, page 19). The less time spending models (50 stress periods) were run for different values of activation energy (*Ea*) to know its influence on the biodegradation. First of all, it was necessary to find out the activation

energy of my basic model. For that purpose, I compared Arrhenius equation for two different rate constants of any two temperatures and calculated activation energy:

$$Ea = \ln \frac{k_1}{k_2} \cdot \frac{R \cdot T_1 \cdot T_2}{T_1 - T_2} \tag{19}$$

where:

Ea	is the activation energy,
T_1, T_2	are the temperatures,
k_1	is the reaction rate constant for the temperature T_1,
k_2	is the reaction rate constant for the temperature T_2 and
R	is the universal gas constant (R = 8.314 J mol^{-1} K^{-1}).

The result for activation energy of PCE is around 62 kJ/mol and for TCE around 51 kJ/mol. These values were used to recalculate reaction rate constants for different activation energies, 100 and 20 kJ/mol, using the equation 20:

$$k_2 = \frac{k_1 \cdot e^{-Ea_2 / RT_2}}{e^{-Ea_1 / RT_1}} \tag{20}$$

where:

Ea_1	is the activation energy from previous calculation (62 kJ/mol),
Ea_2	is the new activation energy (20 and 100 kJ/mol),
T_1, T_2	are the temperatures,
k_1	is the reaction rate constant for the activation energy Ea_1 and temperature T_1,
k_2	is the reaction rate constant for the activation energy Ea_2 and temperature T_2 and
R	is the universal gas constant (R = 8.314 J mol^{-1} K^{-1}).

From this equation, I get the values of reaction rate constant for activation energy 100 and 20 kJ/mol, which were used in the model to see how lower and higher activation

energy influences biodegradation of chlorinated hydrocarbons. The new equations of reaction rate constants for Ea_1 = 100 kJ/mol are shown below.

The equation for PCE:

$$k^{PCE} = 3 \cdot 10^{-16} \cdot e^{0,1484 \cdot T} \quad (21)$$

where:

k^{PCE} is the reaction rate constant of PCE [1/d] and

T is the temperature [°C].

The equation for TCE:

$$k^{TCE} = 5 \cdot 10^{-18} \cdot e^{0.1484 \cdot T} \quad (22)$$

where:

k^{TCE} is the reaction rate constant of TCE [1/d] and

T is the temperature [°C].

The new equations of reaction rate constants for Ea_1 = 20 kJ/mol are following.
The equation for PCE:

$$k^{PCE} = 0.6236 \cdot e^{0.0297 \cdot T} \quad (23)$$

where:

k^{PCE} is the reaction rate constant of PCE [1/d] and

T is the temperature [°C].

The equation for TCE:

$$k^{TCE} = 0.0087 \cdot e^{0.0297 \cdot T} \quad (24)$$

where:

k^{TCE} is the reaction rate constant of TCE [1/d] and

T is the temperature [°C].

2.4 Analytical solution for first order reaction

The analytical solution of contaminant distribution of PCE and TCE in the time for first order reaction was calculated to verify the correctness of numerical models. Equations 25 and 26 hold for PCE and TCE, respectively. When solving the problem, mass of the component contained in the aquifer was substituted for its concentration in order to make the computation easier.

$$C^{PCE} = C_0^{PCE} \cdot e^{-k^{PCE}t} \tag{25}$$

where:

C^{PCE} is concentration of PCE in the time,

C_0^{PCE} is the initial concentration of PCE,

k^{PCE} is the first order rate constant of PCE in ATES system and

t is the time.

$$C^{TCE} = \frac{F_{PCE}^{TCE} \cdot k^{PCE} \cdot C_0^{PCE}}{k^{TCE} - k^{PCE}} \cdot \left(e^{-k^{TCE}t} - e^{-k^{PCE}t} \right) \tag{26}$$

where:

C^{TCE} is the concentration of TCE,

F_{PCE}^{TCE} is the stoichiometry coefficient = 1,

k^{PCE} is the first order rate constant of PCE,

C_0^{PCE} is the initial concentration of PCE,

k^{TCE} is the first order rate constant of TCE and

t is time.

The reaction rate constants of PCE and TCE can be expressed by modified Arrhenius equation provided the residence times of warm water and cold water are approximately equal in the ATES system. (Hartog, 2011):

$$k_{ATES} = \frac{k_{hot} + k_{cold}}{2} = \frac{A\left(e^{Ea/RT_{hot}} + e^{Ea/RT_{cold}} \right)}{2} \qquad (27)$$

where:

k_{ATES} is the reaction rate constant for the ATES system,

k_{hot} is the reaction rate constant at the temperature T_{hot} in the hot well,

k_{cold} is the reaction rate constant at the temperature T_{cold} in the cold well,

A is the pre – exponential factor,

E_a is the activation energy of the reaction [J/mol]

R is the universal gas constant (R = 8.314 J mol^{-1} K^{-1}),

T_{hot} is the temperature in the hot well and [K]

T_{cold} is the temperature in the cold well [K].

The modified Arrhenius equation (Hartog, 2011) has to be used in such ATES systems where the residence times of warm and cold water are different. The Uithof ATES system can serve as an example as the periods of pumping into its warm well and its cold well are 64 % and 35 % of the whole time.

$$k_{ATES} = 0.6535 \cdot k_{hot} + 0.3365 \cdot k_{cold} \qquad (28)$$

where:

k_{ATES} is the rate constant of a particular kinetic reaction in an ATES system,

k_{hot} is the reaction rate constant at the temperature T_{hot} in the hot well and

k_{cold} is the reaction rate constant at the temperature T_{cold} in the cold well.

2.5 Modelling of oxidation-reduction conditions

Using the program PHT3D to model mixing oxidation-reduction zones and dependence between oxidation-reduction conditions and biodegradation of chlorinated hydrocarbons has to be preceded by using the program PHREEQC to model the balance of oxidation-reduction species.

2.5.1 PHREEQC model

The balance was evaluated separately for each one of the oxidation-reduction zones. The zone of denitrification was neglected, because it is not so important for biodegradation of chlorinated hydrocarbons. To make model as simple as possible, I applied equilibrium components determined for each oxidation-reduction zone modelled using the PHREEQC model. The zones and the related components are represented in Table 7.

Table 7: Oxidation-reduction zones and related components modeled using the PHREEQC.

Zone	**Components**
1. Aerobic respiration	O_2, CO_2, Calcite
2. Fe(III) reduction	Siderite, CO_2, Calcite
3. Sulphate reduction	Pyrite, CO_2, Calcite
4. Methanogenesis	CH_4, CO_2, Calcite

The PHREEQC output values of concentrations were used in the PHT3D as initial concentrations when modelling the ATES system without contamination by chlorinated hydrocarbons.

2.5.2 Solving problems in PHT3D

In this part of project I tried to simulate biodegradation of chlorinated hydrocarbons under combined oxidation-reduction conditions using the PHT3D. Initially I used the outputs of oxidation-reduction conditions from PHREEQC together with chlorinated

hydrocarbons as input data in the PHT3D model to get the the dependence of the chlorinated hydrocarbons on the oxidation-reduction conditions. In the next step, the aim was to include *Eh*, a characteristic value of oxidation-reduction conditions, into the database file in order to know whether the degradation occurs or not in the mixed water. As was mentioned, that chlorinated hydrocarbons are degraded only under specific oxidation-reduction conditions. PCE decays to TCE in all oxidation-reduction conditions except aerobic. The degradation of TCE to DCE undergo in iron reduction and in stronger reducing environment. Dechlorination of DCE to VC occurs under sulphate but more easily under methanogenesis conditions. For these oxidation-reduction conditions, I found in literature the values of *Eh* corresponding to particular conditions as shown in Table 8 (Langevoort, 2009).

Table 8: *Eh* ranges for oxidation-reduction conditions.

Redox conditions	***Eh* range (mV)**
Aerobic	> 250
Denitrification	100 – 250
Fe and Mn reduction	0 – 100
Sulphate reduction	-200 – 0
Methanogenesis	< -200

As the program SEAWAT works only with the $p\varepsilon$ values, it was necessary to convert values of *Eh* to $p\varepsilon$, (equation 29) (DeLaune and Reddy, 2005):

$$p\varepsilon = \frac{Eh(mV)}{59} \tag{29}$$

where:

$p\varepsilon$ is the relative electron activity and

Eh is the oxidation-reduction potential.

The values of $p\varepsilon$ for each step of degradation of chlorinated hydrocarbons are given in Table 9 (page 46).

Table 9: Ranges of $p\varepsilon$ for each degradation step of chlorinated hydrocarbons.

Degradation step	***pε* range**
PCE → TCE	< 4.237
TCE → DCE	< 1.695
DCE → VC	< 0
VC → ethylene	< - 3.39

I used these given values to define oxidation-reduction conditions that are required for the biodegradation of particular chlorinated hydrocarbons.

2.6 Model of heat transport in FEFLOW

To complete the project of transport of contamination by chlorinated hydrocarbons within the ATES system, the model of heat transport was set up, because heat has an important influence on density, specific heat, and thermal conductivity within the aquifer with ATES system.

Heat transport was modelled in the program FEFLOW, because the FEFLOW is more suitable for heat transport modelling. In the first step, basic Zuurbier's model (Zuurbier *et al.*, 2013) with ATES system obtained by means of the MODFLOW was converted into the FEFLOW. As this part of my work was focused on the heat transport modelling, it was not necessary to include the contaminant transport of chlorinated hydrocarbons.

Due to the lack of measured heat characteristics, I used the values recommended in the FEFLOW manual. The required dispersivities were known from measurements. A summary of input values for heat transport model is shown in the Table 10 (page 47). I used temperature of each well as a function of time for the heat transport boundary conditions of the Dirichlet type.

Table 10: Values of heat characteristic of aquifer.

	Value	**Unit**
Porosity	0.35	-
Volumetric Heat capacity of fluid	4.2	10^{-6} J/m^3/K
Volumetric Heat capacity of solid	2.52	10^{-6} J/m^3/K
Heat conductivity of fluid	0.65	J/m/s/K
Heat conductivity of solid	3	J/m/s/K
Longitudinal dispersivity	1	m
Transversal dispersivity	0.1	m

3 Results

3.1 Temperature in the time

During the modelled period, the time intervals of cold water pumping and hot water pumping change regularly. The effect of the pumping results in gradual changing of temperature in the whole domain. As shown in Figures 5 and 6 (page 49) we can see the temperature changes over the time in each particular well. For plotting these charts, I chose data from seventh layer (Table 2, page 30). In Figure 5 we can see temperature in the cold well, in Figure 6 (page 49) temperature of the hot well. The temperature of water pumped to the cold well is 8°C, the temperature of the water pumped to the hot well is 16°C. The lowest peaks in Figure 5 with temperature in the cold well reflect the injection of cold water from the cooling system. The highest values in Figure 6 (page 49) with temperature in warm well indicate injection of warm water from the heating system.

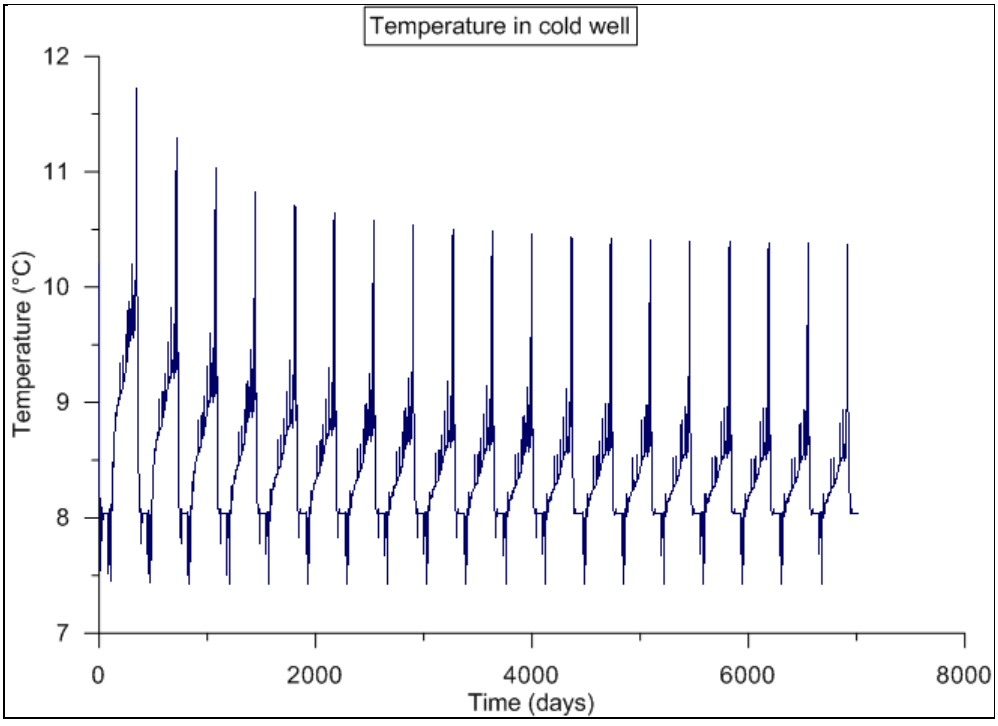

Figure 5: The temperature changes in seventh layer of the cold well during 2000 days.

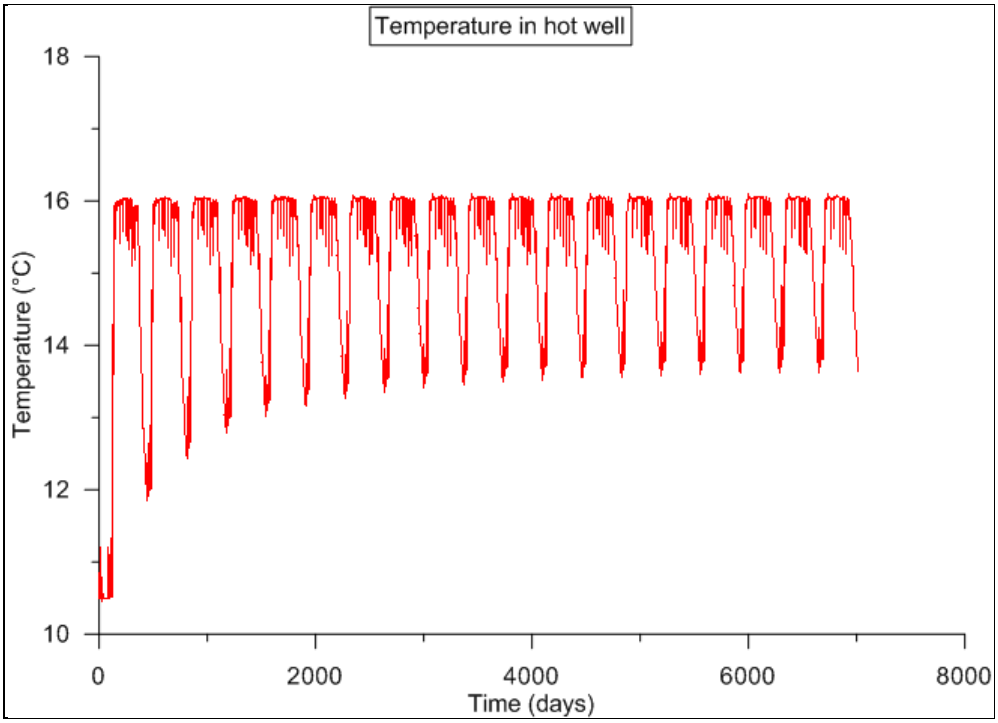

Figure 6: The temperature changes in the seventh layer of hot well during 2000 days.

3.2 Comparison of the models with and without temperature dependence

3.2.1 Models with first order reaction rate constants

In Figures 7 and 8 (page 50 and 51) we can see the charts of PCE and TCE mass versus time of ATES systems working at temperatures 8 and 16°C compared with bigger differences in the temperature (3 and 25°C or 5 and 80°C). Scenarios without the temperature dependence give the same total mass of PCE and TCE in the aquifer because the rate constants are independent of temperature, thus the bigger differences between them have no influence on the degradation.

Figures 7 and 8 show that the influence of the temperature on the biodegradation is significant only for the larger differences between the temperatures of the cold and hot well. It was found that in the region of real temperatures in the ATES system at Uithof, the effect of temperature on the biodegradation is more or less negligible when compared with the results obtained without taking the temperature dependence into

account. Under the conditions of constant temperature, the mass of PCE decrease almost as quickly as in the case of the changing temperature. In Figure 7, we can also see that the exponential behaviour between reaction rate constant and temperature is only visible if the process is accompanied with larger differences in the temperature as e.g. 5 and 80°C. Just in the case of high temperature (80°C) of the hot well, the starting time of the injection of hot water is distinctly visible. This appears approximately at the 140-th day when the degradation starts to be faster due to the rising temperature of the aquifer.

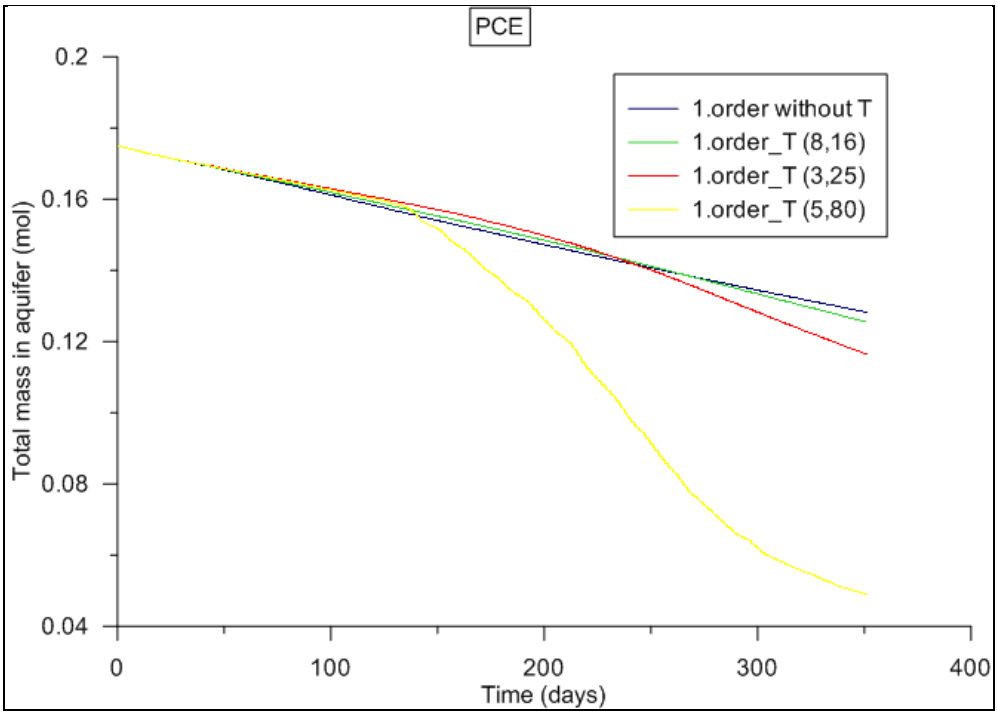

Figure 7: The result for PCE total mass in aquifer of first order models without and with temperature dependence.

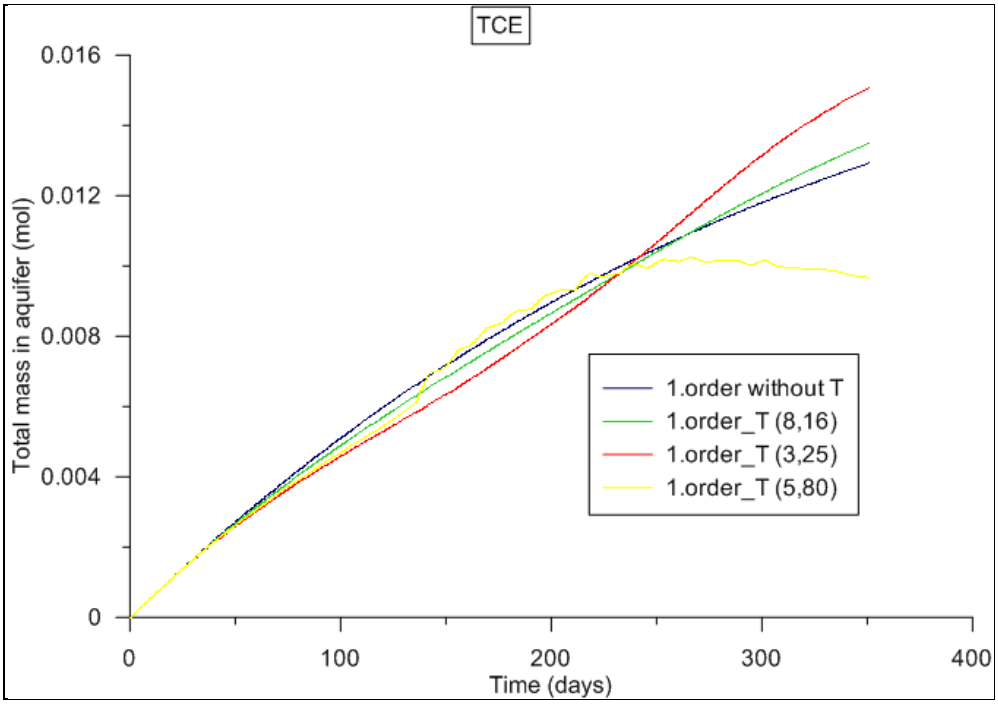

Figure 8: The result for TCE total mass in aquifer of first order models without and with temperature dependence.

3.2.2 Models with zero order reaction rate constants

When modelling the zero order reactions, the results depend on the chosen value of reference concentration. We chose the reference concentration value 10^{-6} g/l in our model. At this reference concentration result of PCE is more or less the same for first and zero order reactions (Figure 9, page 52). In Figure 10 (page 52) we can see, that the choice of reference concentration affects the results significantly in the case of zero order reactions.

It was found that models with zero order reactions and with the higher differences in the temperature of hot and cold well give the same result as the models of first order reaction (Figure 11 and 12 on page 53). The temperature in the ATES system does not play very important role in the biodegradation of chlorinated hydrocarbons (see Figures 11 and 12, page 53).

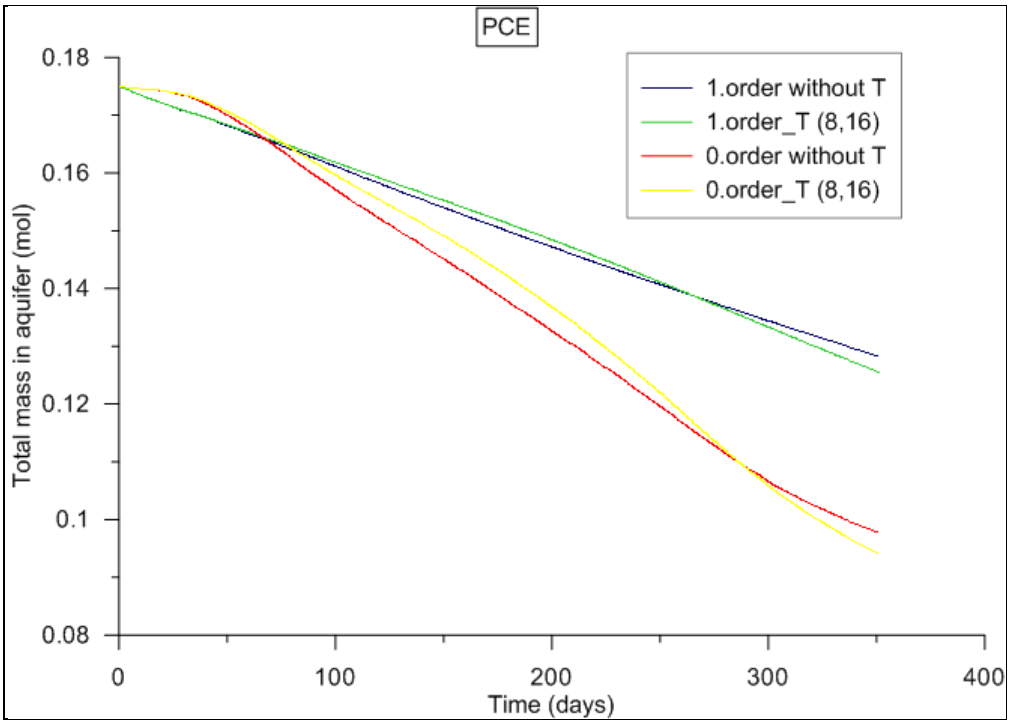

Figure 9: The result for PCE models of first order and zero order reactions with reference concentration equal 10^{-6}.

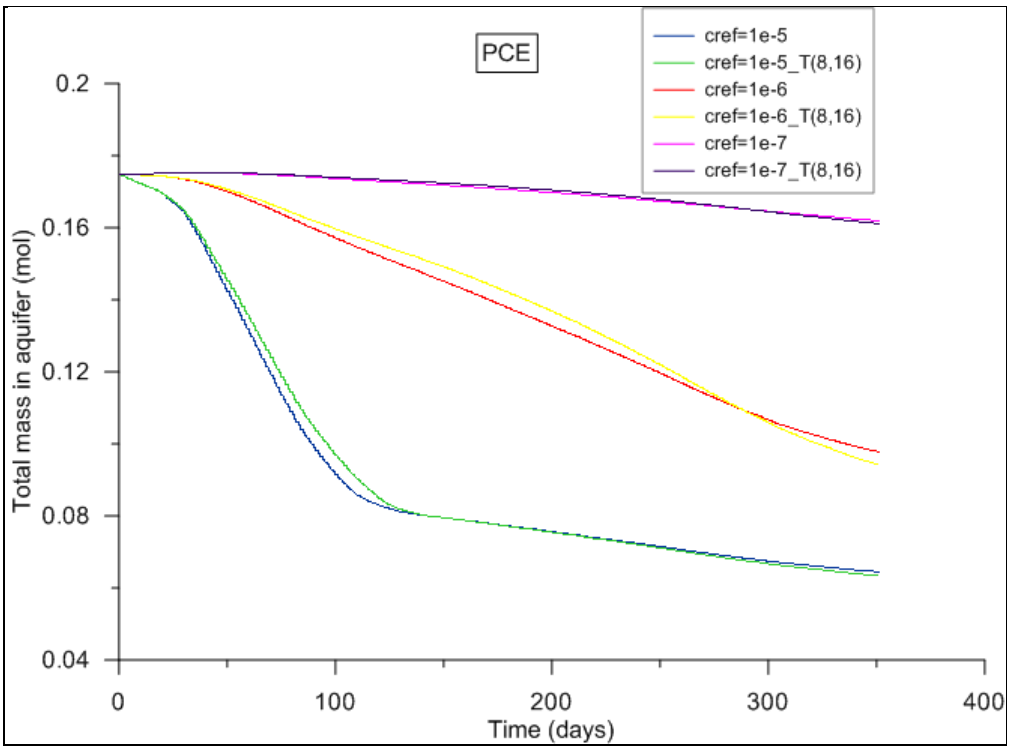

Figure 10: The result of PCE from models with different reference concentration.

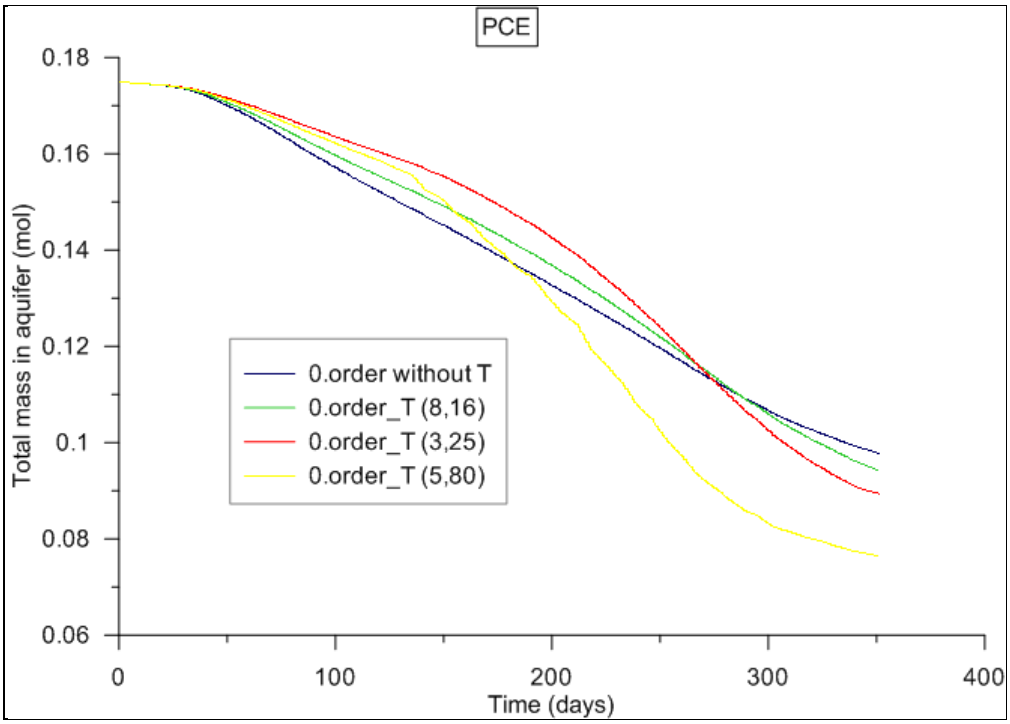

Figure 11: The result for PCE total mass in aquifer of the models with zero order reactions with different temperatures of hot and cold well.

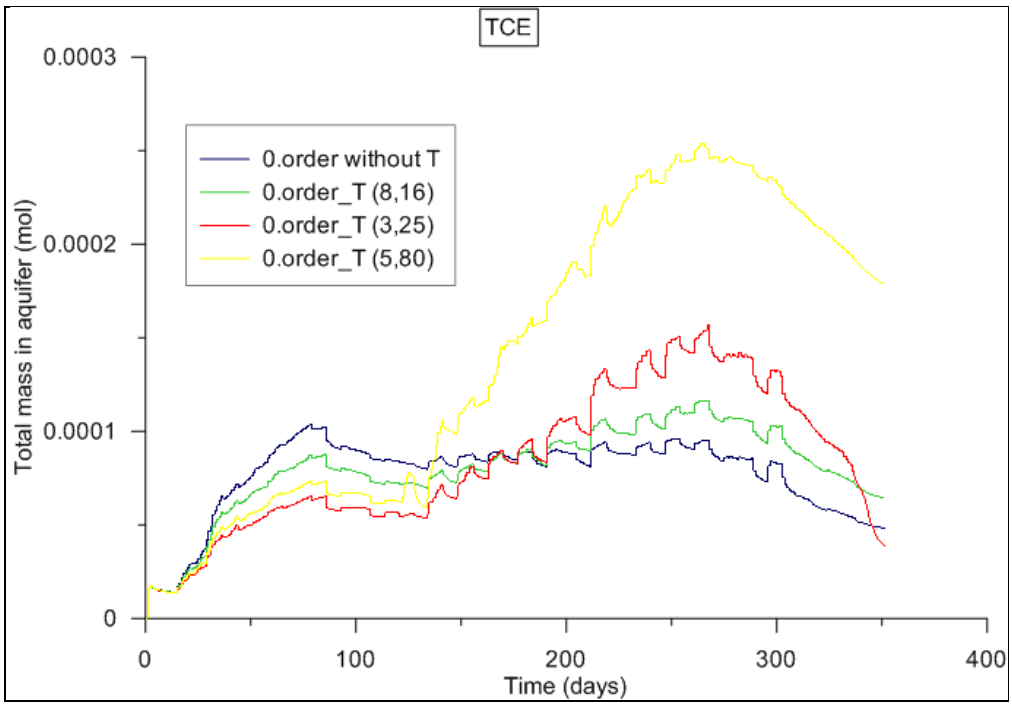

Figure 12: The total mass in aquifer as a result of the models with zero order reactions with different temperatures of hot and cold well.

The presented results show that the output from models of zero order reactions with the different temperatures of hot and cold well is mainly dependent on the chosen value of reference concentrations (Figure 10, 11, and 12 on the pages 52 and 53). The value of reference concentration equal to 10^{-6} g/l was used in all other models.

3.2.3 Long time models with first and zero order reactions

For the long time model, in our case 19 years, the total mass of species in aquifer appears almost independent of temperature (Figure 13). This is valid for the first order as well as for the zero order reaction.

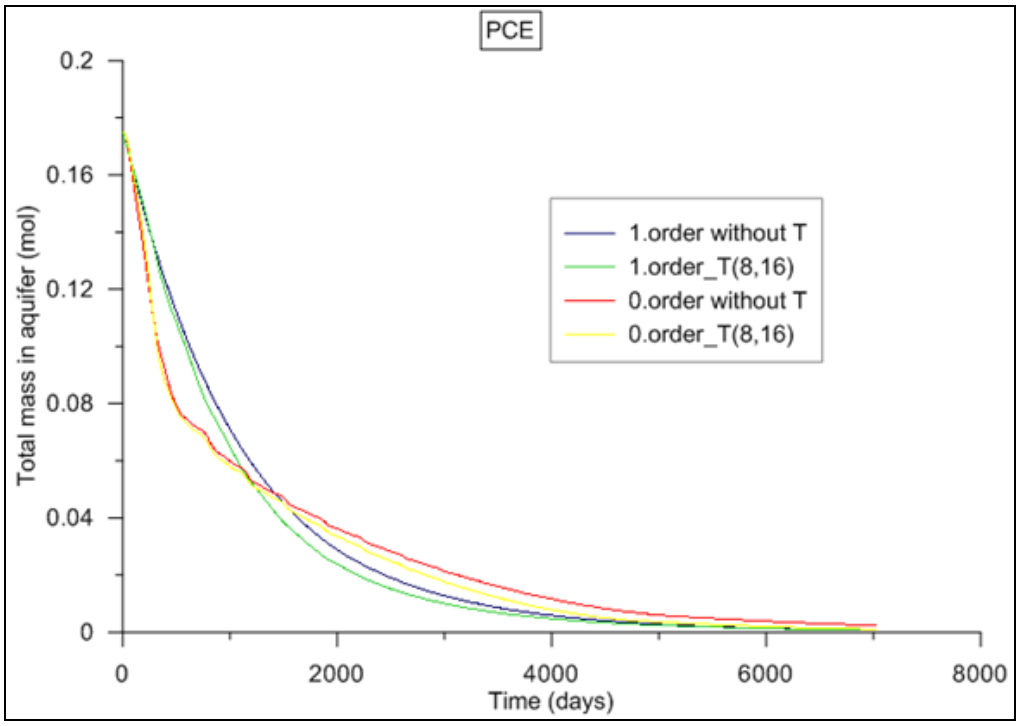

Figure 13: Results of long models (19 years) with first and zero order reaction independent and dependent on the temperature.

3.3 Scenarios with and without ATES system

The results of my models indicate a great impact of the ATES system on biodegradation in case of zero order reactions only. The biodegradation proceeds slowly in the situation of zero order reactions without the ATES system. If so, the contamination remains in ground water for a very long time. The more visible degradation occurs in the case of zero order reactions in the aquifer with the ATES system. This is caused by spreading of the contaminant into the bigger volume of sediment. On the other hand, the result for the zero order reaction is dependent on the choice of the reference concentration.

In the case of first order reactions, the results are same for versions with and without ATES system especially for PCE and TCE. The differences are more visible only for DCE and VC.

Following figures show the results of models for PCE (Figure 14, page 56), TCE (Figure 15, page 56), DCE (Figure 16, page 57) and VC (Figure 17, page 57) with and without ATES system. Results obtained for the scenarios with first and zero order reaction including and excluding the ATES system are depicted in Figures 14, 15, 16 and 17 (on the pages 56 and 57). My results of this part of the project agree more or less with the previous study made by K. G. Zuurbier (Zuurbier *et al.*, 2013), who presents similar conclusions.

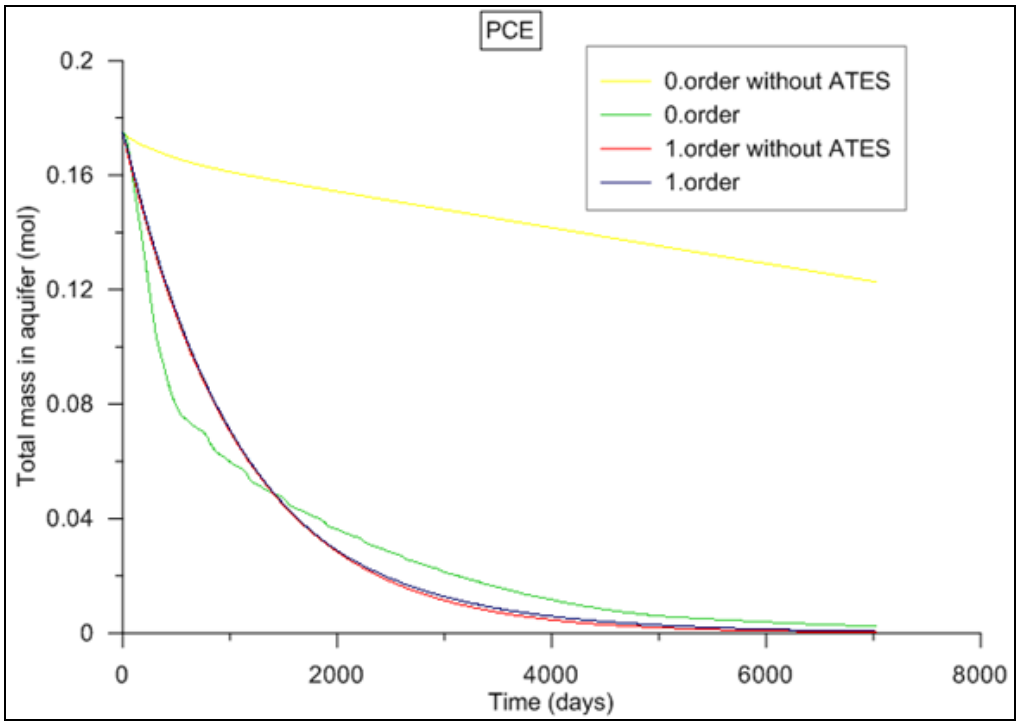

Figure 14: The total mass in aquifer of PCE as a result of models with and without ATES system.

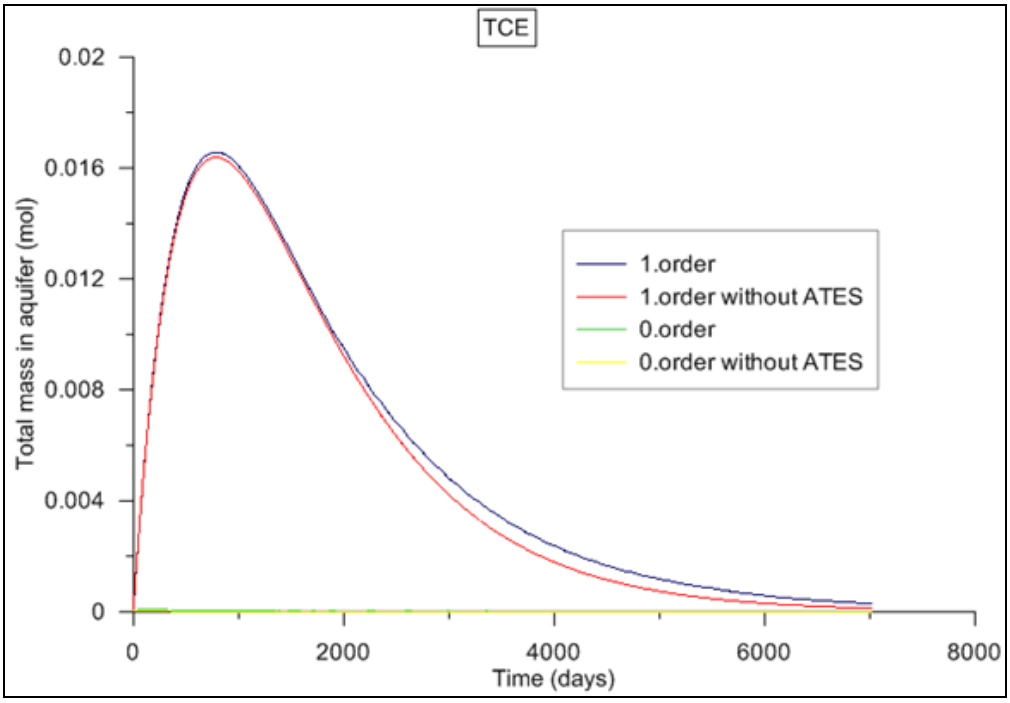

Figure 15: The total mass in aquifer of TCE as a result of models with and without ATES system.

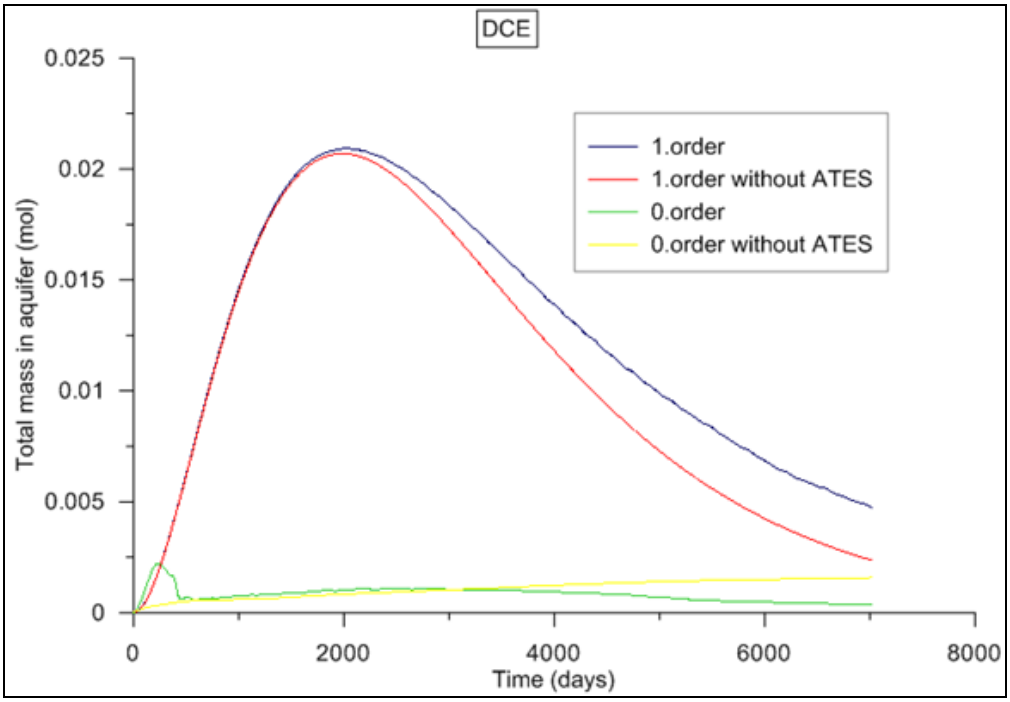

Figure 16: The total mass in aquifer of DCE as a result of models with and without ATES system.

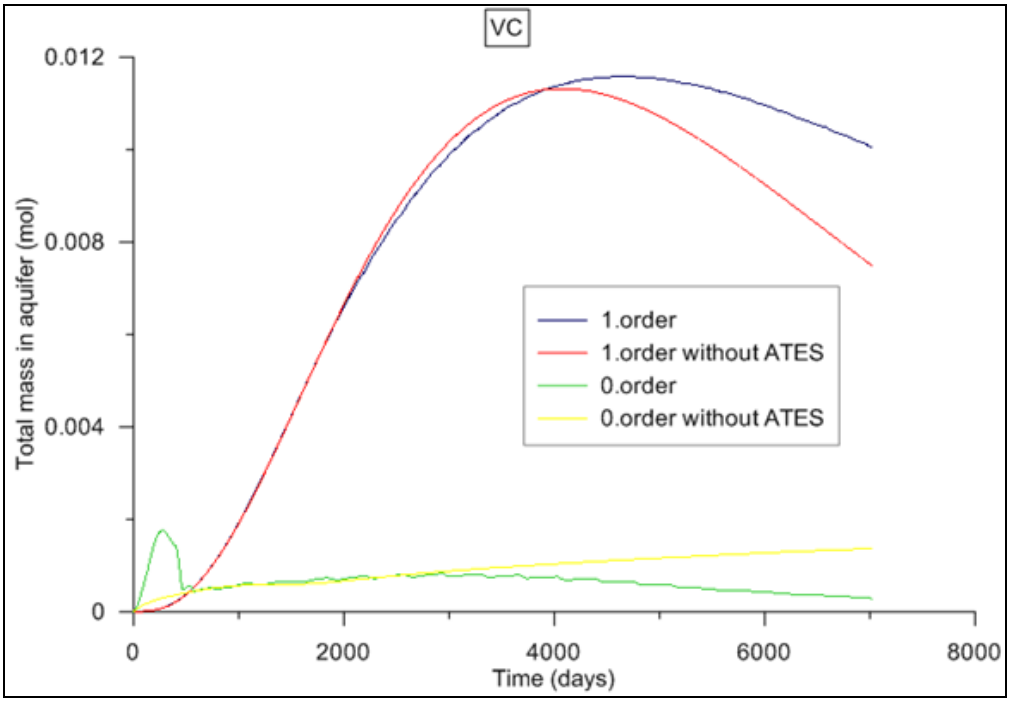

Figure 17: The total mass in aquifer of VC as a result of models with and without ATES system.

3.4 Models with different values of activation energy

The activation energy influences the reaction rate constant, so it influences also the speed of the degradation. For a large value of activation energy (Ea = 100 kJ/mol) the reaction rate constant is so small that the speed of biodegradation becomes almost zero. Opposite results were obtained for the small activation energy (Ea = 20 kJ/mol), the value for the reaction rate constant is large and the biodegradation goes very fast. In Figure 18, we can see the results of PCE simulations with different activation energies. The outputs for large and small activation energies are same for first order as well as for zero order reactions.

The scenario with activation energy Ea = 20 kJ/mol was run also for long time model with 988 stress period (Figure 19, page 59).

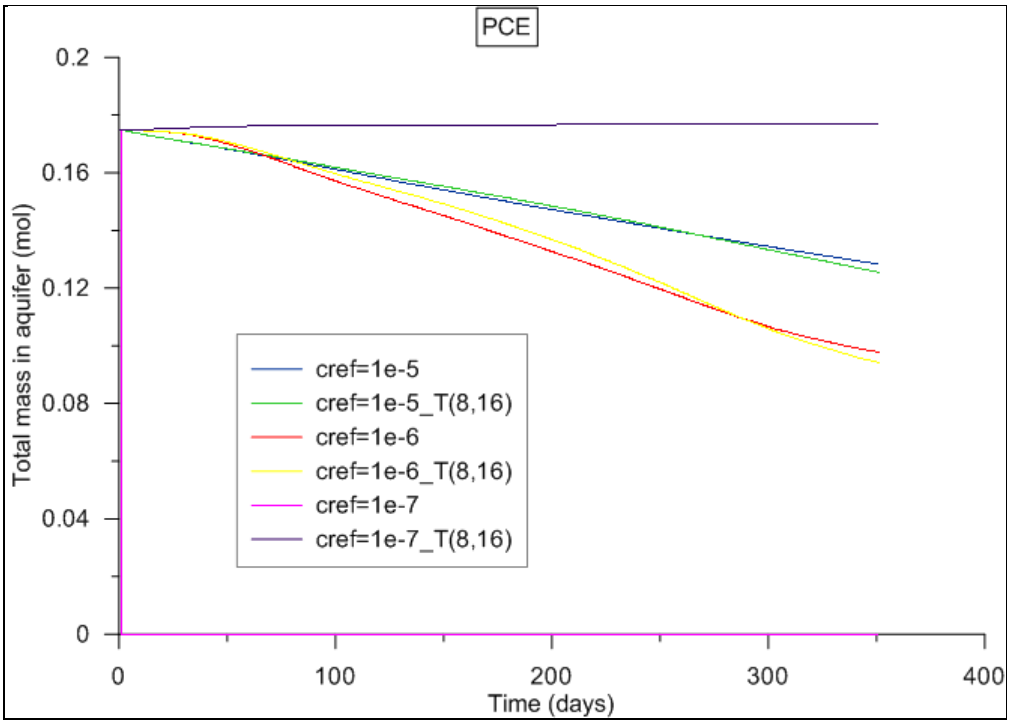

Figure 18: Results of PCE from models with different value of activation energy.

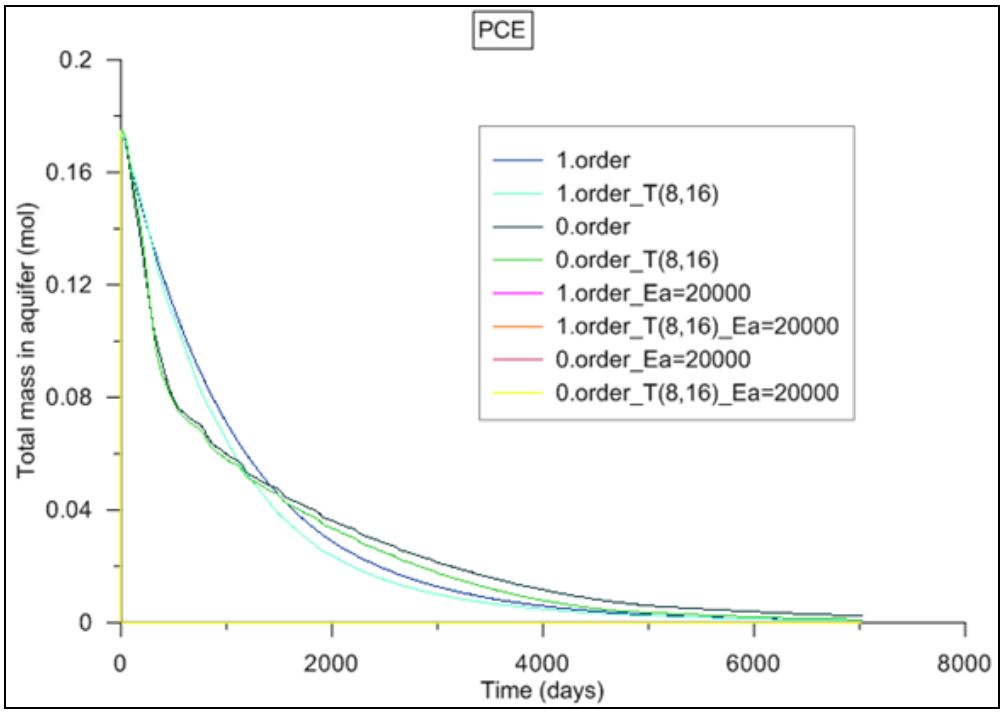

Figure 19: Mass of PCE from long model with activation energy Ea = 20 kJ/mol.

In Figure 18 (page 58) and 19 we can see that, for activation energy Ea = 20 kJ/mol, the degradation is same for all scenarios (just the yellow line is seen, the others are hidden below it). The degradation is so fast that the concentration reaches immediately zero.

3.5 Comparison of numerical and analytical solution

In order to demonstrate the reliability of numerical models, solutions of two PCE and TCE concentration models were repeated analytically. The obtained numerical and analytical results are compared in Figure 20 on the page 60 for PCE and in Figure 21 for TCE on the page 60.

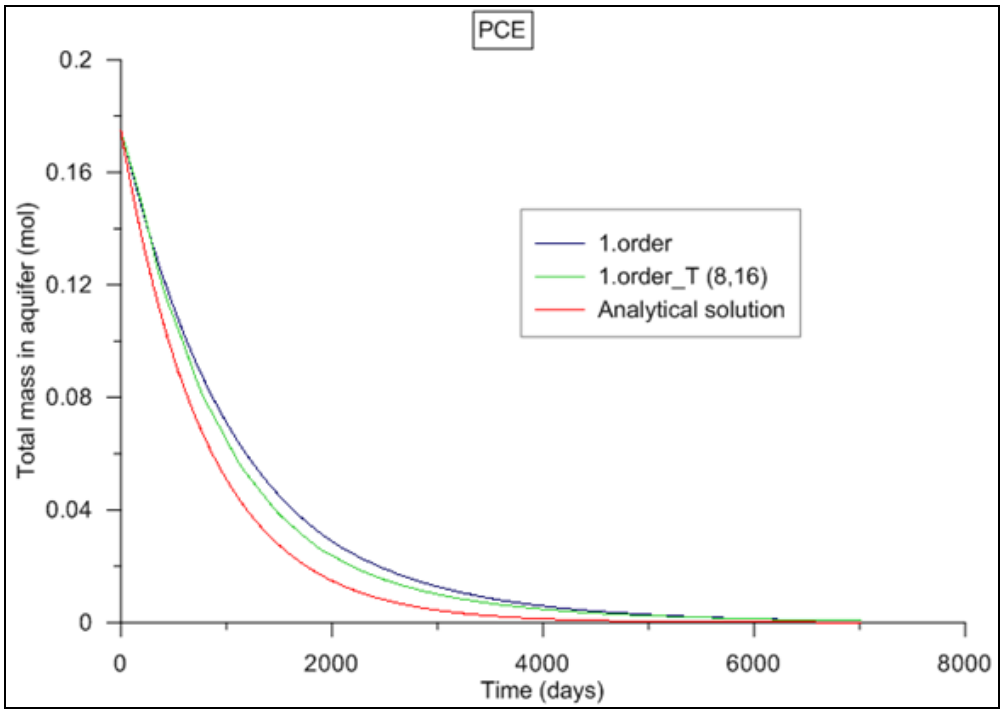

Figure 20: Comparison of numerical and analytical solution of PCE.

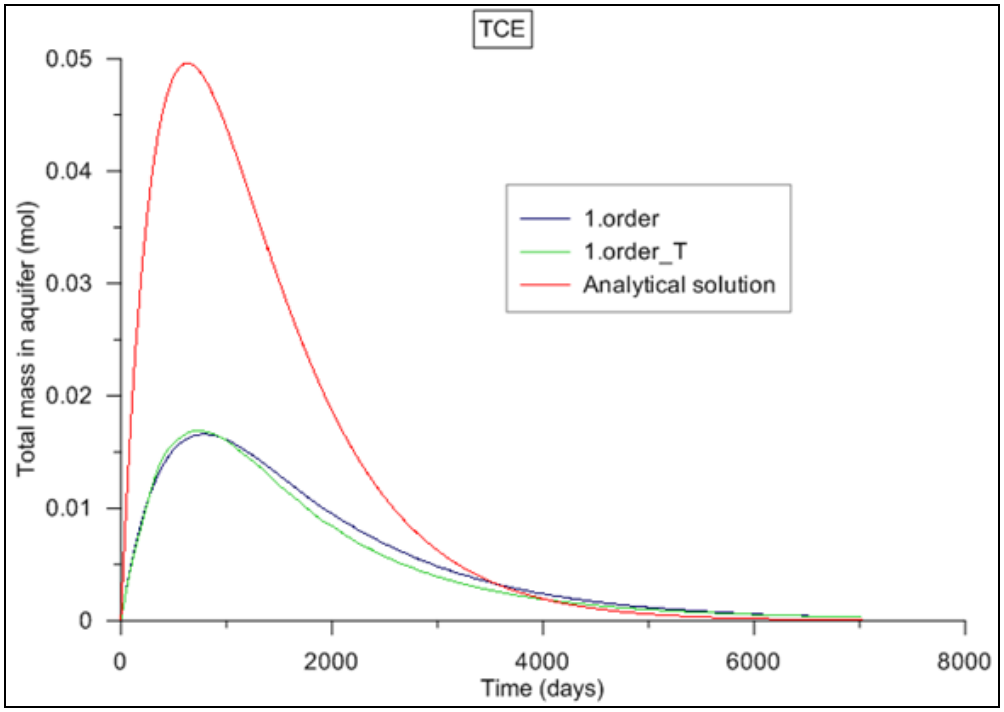

Figure 21: Comparison of numerical and analytical solution of TCE.

It can be seen in Figures 20 and 21 on the page 60 that the degradation calculated analytically is faster than that given by the numerical model. It can be explained by the chosen value of the reaction rate constant used in analytical solution. The chosen value, derived as the average of the hot and cold well constants, corresponds to the temperature around 12°C. The temperature within the aquifer is lower than this value and the degradation goes slower.

Similar differences between numerical and analytical solutions are visible in Figures 22, 23, 24 and 25 on the page 62 and 63, where the results of numerical and analytical models are plotted, this time for higher differences in temperature, the cold well has a temperature 3°C and 5°C and the hot well 25°C and 80°C respectively. In the first version, with the temperature of the cold well 3°C and the hot well 25°C, the temperature 14.2°C corresponds to the reaction rate constant used in analytical solution. In the second version with the temperature of the cold and hot well 5°C and 80°C respectively, the value of the reaction rate constant corresponds to 38.3°C. The real temperatures of the aquifer are probably lower than these values.

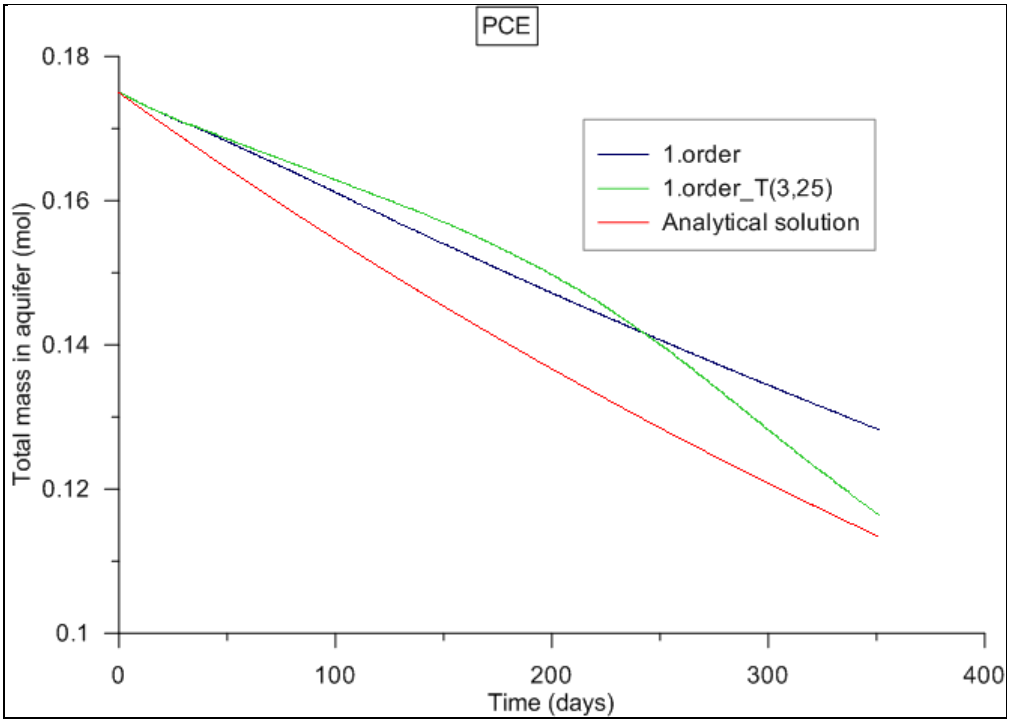

Figure 22: The comparison of numerical and analytical models of PCE mass with higher differences in the temperature (3, 25°C).

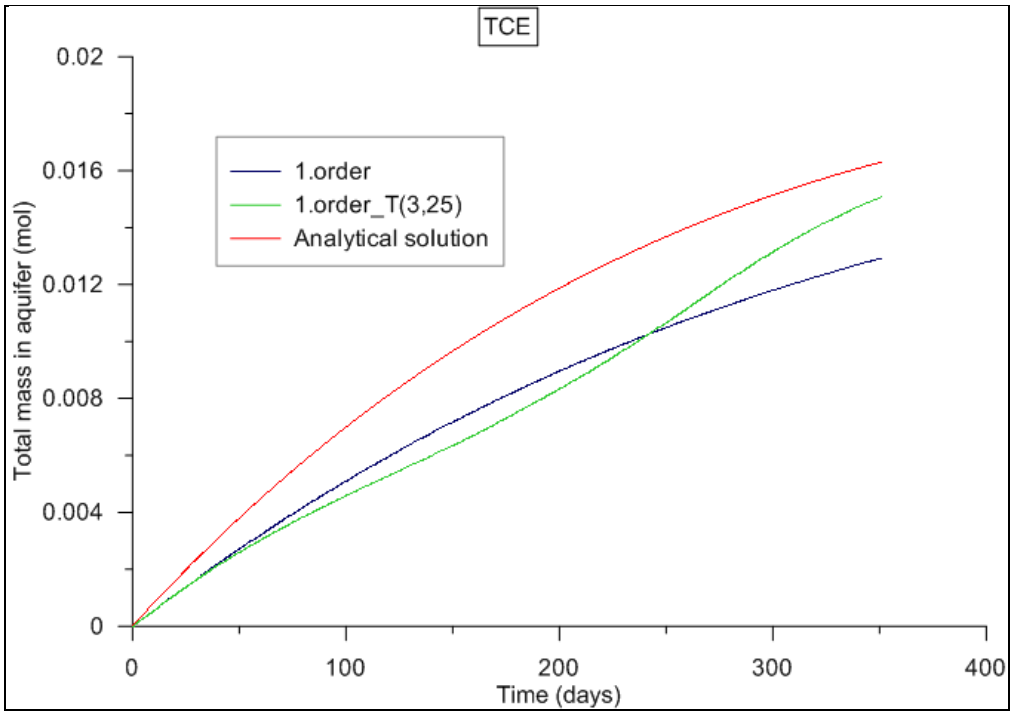

Figure 23: The comparison of numerical and analytical models of TCE mass with higher differences in the temperature (3, 25°C).

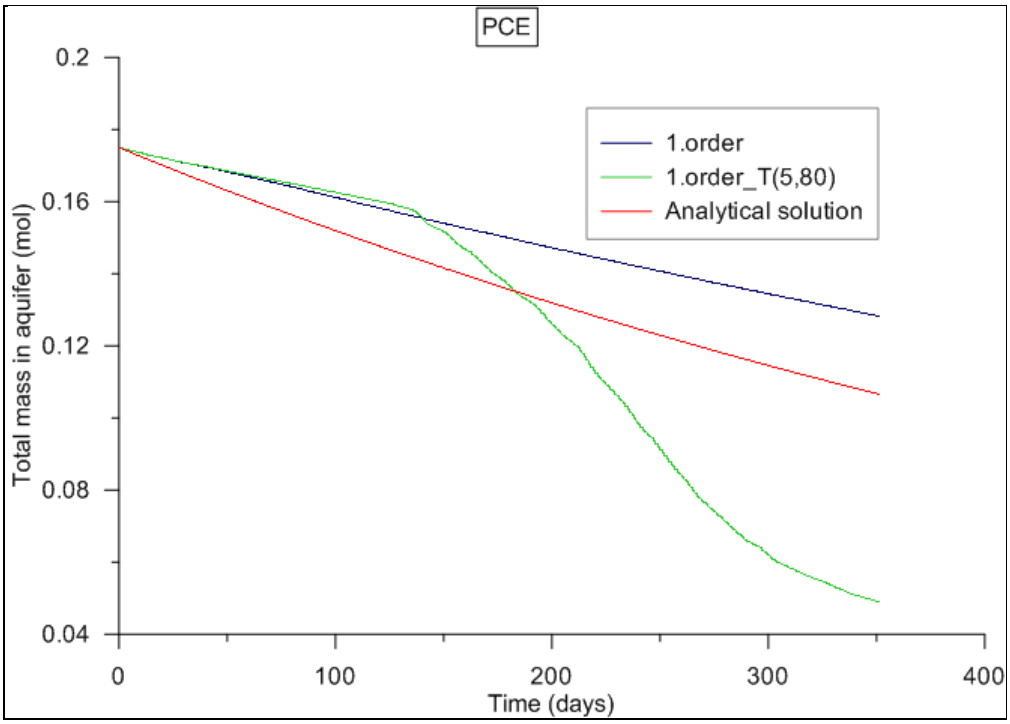

Figure 24: The comparison of numerical and analytical models of PCE mass with higher differences in the temperature (5, 25°C).

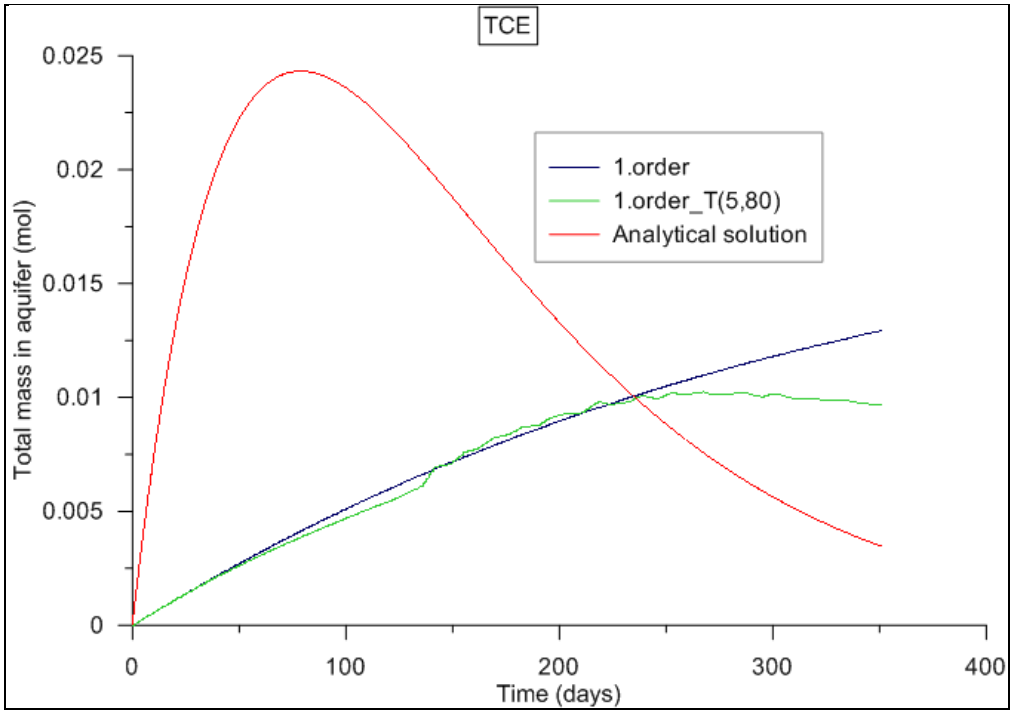

Figure 25: The comparison of numerical and analytical models of TCE mass with higher differences in the temperature (5, 80°C).

3.6 Models of oxidation-reduction conditions

The dependence of biodegradation of chlorinated hydrocarbons on mixed oxidation-reduction conditions within ATES system was modelled with respect to coupling oxidation-reduction potential with chlorinated hydrocarbons. Results of the models were compared with outputs from models without oxidation-reduction dependence to determine the influence of mixing oxidation-reduction conditions on the biodegradation of chlorinated hydrocarbons. From Figures 26, 27, 28 and 29 on the page 64 and 65 we can see, that the biodegradation of chlorinated hydrocarbons is much more significant if the models include oxidation-reduction conditions than without them. This is valid for all chlorinated hydrocarbons included in the models: PCE, TCE, DCE as well as VC. It can be seen from these results that the temperature of the ATES system, which is 8°C of cold water and 16°C of hot water, is not important for biodegradation of chlorinated hydrocarbons, but the inclusion of mixed oxidation-reduction conditions influences the biodegradation significantly.

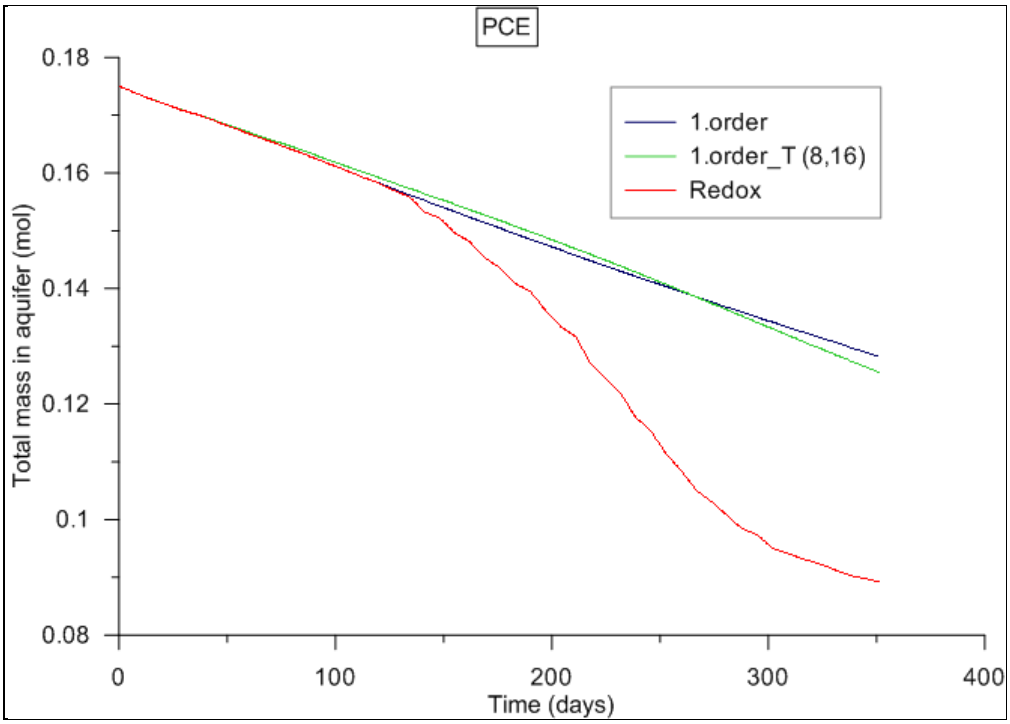

Figure 26: Projection of dependence of PCE mass in aquifer on oxidation-reduction conditions with PCE mass in aquifer from previous models without oxidation-reduction conditions.

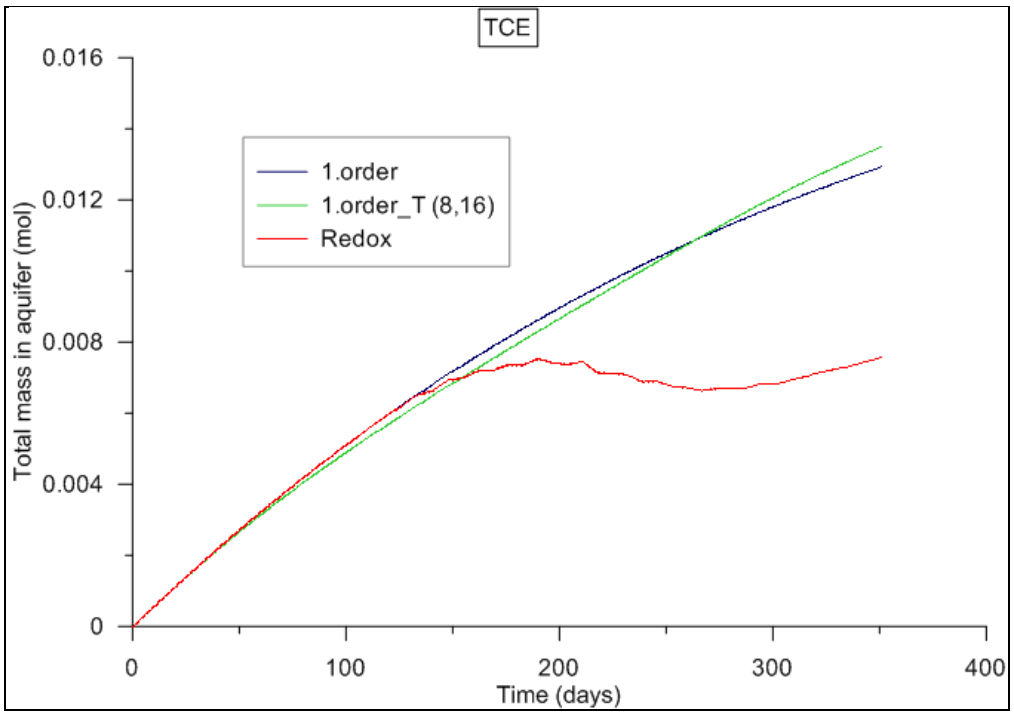

Figure 27: Projection of dependence of TCE mass in aquifer on oxidation-reduction conditions with TCE mass in aquifer from previous models without oxidation-reduction conditions.

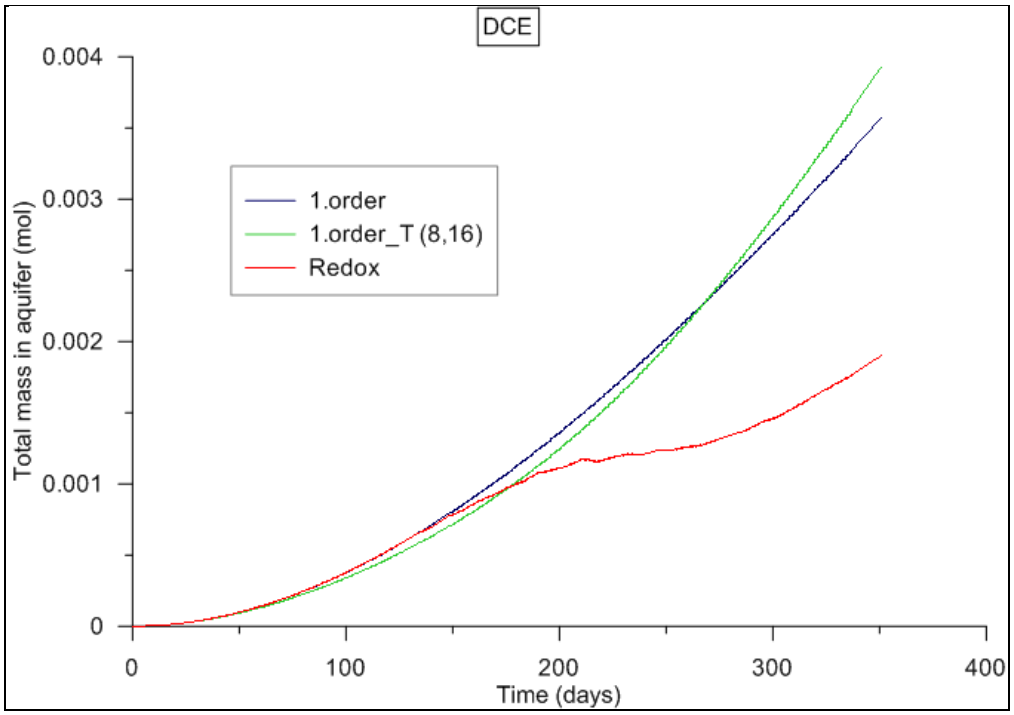

Figure 28: Projection of dependence of DCE mass in aquifer on oxidation-reduction conditions with DCE mass in aquifer from previous models without oxidation-reduction conditions.

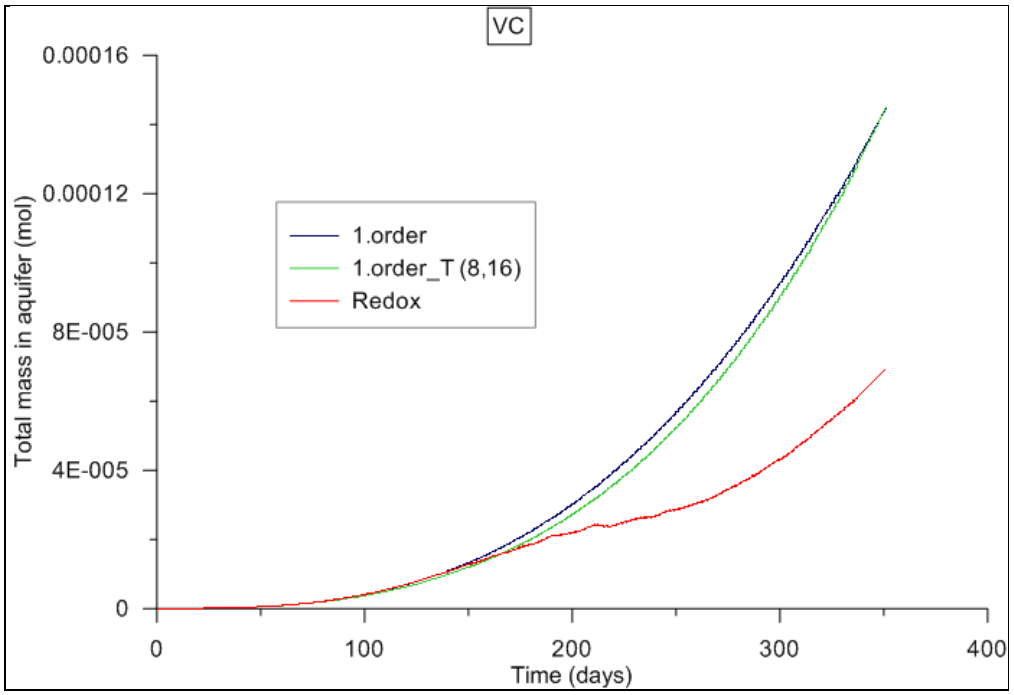

Figure 29: Projection of dependence of VC mass in aquifer on oxidation-reduction conditions with VC mass in aquifer from previous models without oxidation-reduction conditions.

3.7 Model of heat transport

It follows from the results of heat transport model, carried out in the program FEFLOW, that the amount of the transported heat is very small. It confirms the basic assumptions of the idea of the ATES system, which requires either low values of hydraulic and thermal (heat) conductivities or low values of hydraulic and thermal gradients. We can see in Figures 30 and 31 on the page 67, that the injected cold and/or hot water remain in a close neighbourhood of the well during the whole interval of injection.

In the major part of the aquifer, the temperature does not change and holds its initial value of the 10.5°C over the whole 1 year period. The result for the seventh layer is shown in Figure 30, as an example of the temperature distribution in a conductive layer. The results are more or less similar in all other permeable layers. The differences are very small and depend only on the values of hydraulic conductivity.

On the other hand, Figure 31, page 67, shows the temperature distribution in second layer where the hydraulic conductivity is much smaller. The temperature is almost constant (10.5°C) even in the close neighbourhood of the wells

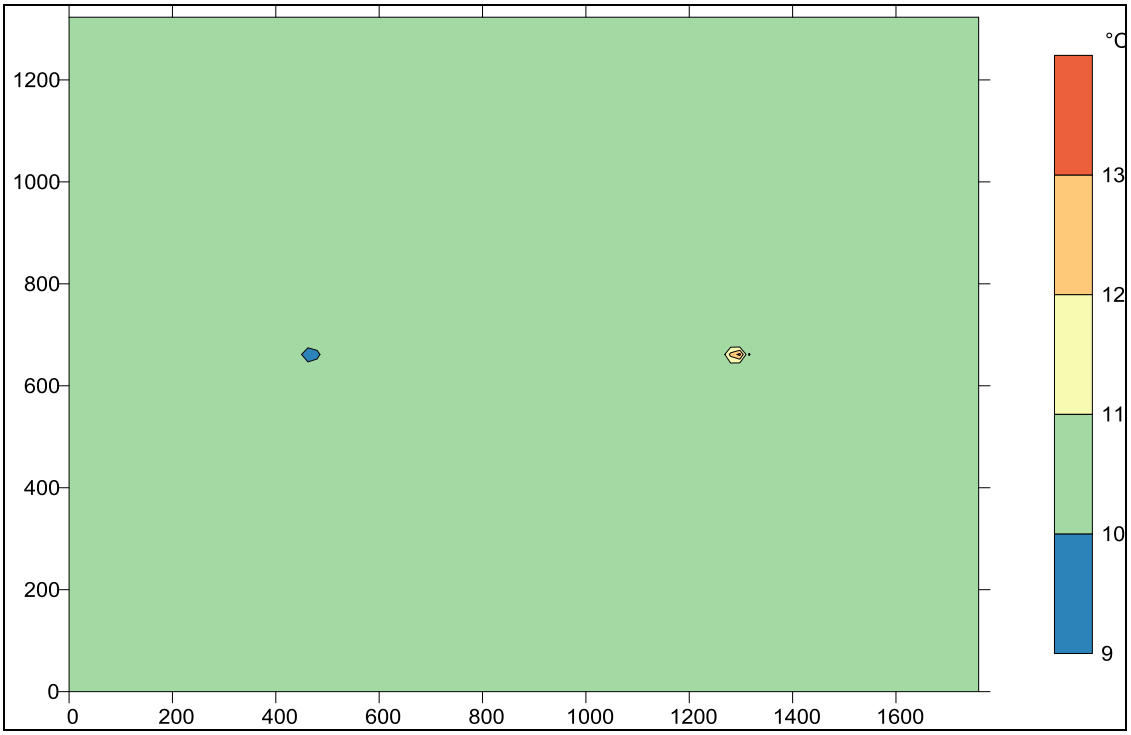

Figure 30: Heat transport in the seventh layer, which represents permeable layers with perforated parts of the wells.

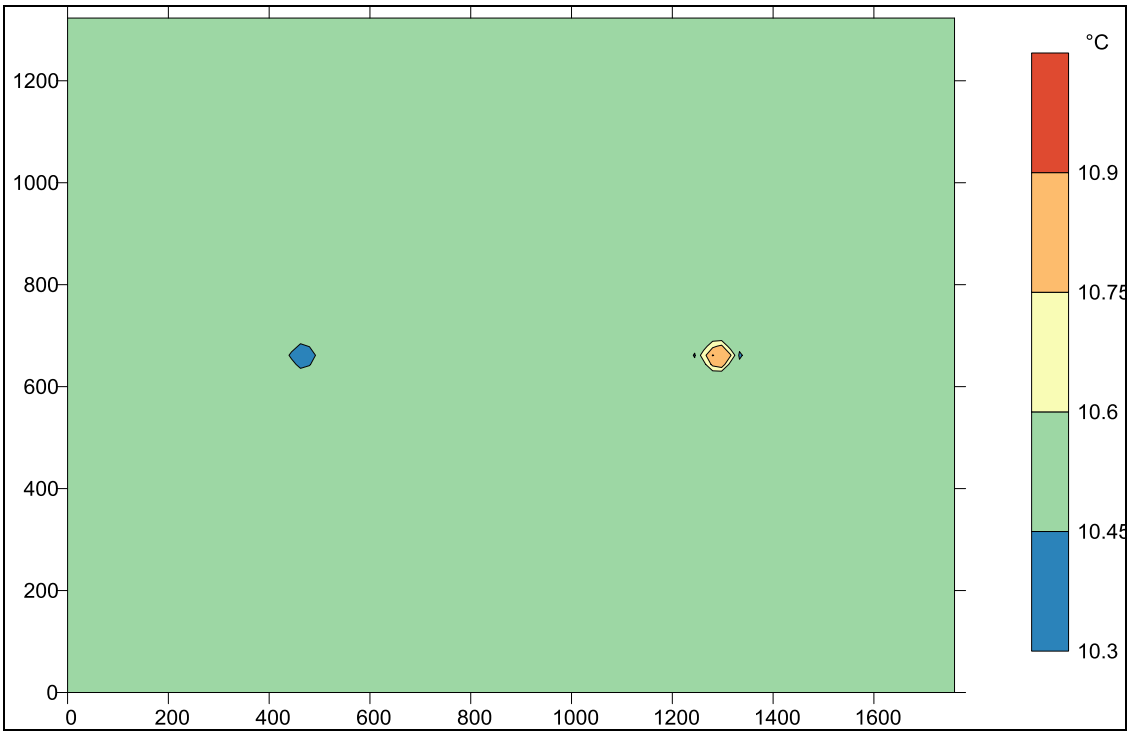

Figure 31: Heat transport in the second layer, in which is no well perforated and it has the lowest hydraulic conductivity.

4 Discussion and conclusion

The ATES system is a technique of heat storing that is nowadays very often used in combination with heating and cooling of buildings. It could have also side effects on ground water system, due to the changes in the temperature and oxidation-reduction conditions in aquifer. The solved project was focused on how these changes could eventually influence the biodegradation of chlorinated hydrocarbons, because their behaviour in ground water depends on the temperature and on the oxidation-reduction conditions.

Several scenarios of relations between ATES systems and biodegradation were formulated and solved in program SEWAT. This study was focused on the dependence of biodegradation of chlorinated hydrocarbons on the temperature and oxidation-reduction conditions in an ATES system.

The variable temperature of the aquifer with ATES system was taken into account for determination of the rate constant. In addition, the influence of the oxidation-reduction conditions was modelled by means of oxidation-reduction potential.

The ATES system is characterized primarily for zero order (sediment limited) reactions. During the presented research, it was found that contamination is spread over a large volume of groundwater due to the pumping and injection of water in the aquifers where the ATES system is applied. This makes the biodegradation faster. Similar results have been obtained by K. G. Zuurbier who concludes, that in case of the sediment-limited degradation (zero order), the contaminants spreading due to the ATES system may strongly increase degradation compared to the situation without the ATES system (Zuurbier, 2013). On the other hand, the contamination can reach those parts of the aquifer, which would be normally clean. In the case of the first order (contaminant limited) reactions, the effect of the ATES system on the rate of chlorinated hydrocarbons degradation is negligible.

It follows from all models with the rate constant dependent on the temperature that the changes of temperature in the aquifer with ATES system (which are normally around 8 – 10°C) do not significantly affect the behaviour of the contamination by chlorinated hydrocarbons. The difference in the temperatures has to be much bigger, minimally 20 – 25°C, to influence the biodegradation of chlorinated hydrocarbons. It means that ATES system does not affect the biodegradation due to changes in the temperature either positively or negatively.

The results of models with different values of activation energy confirm that the biodegradation depends on the activation energy. In addition, its effect on the biodegradation is quite significant, because for the small activation energy (20 kJ/mol) the degradation of chlorinated hydrocarbons is so fast, that the concentration of PCE becomes immediately zero. For the high activation energy (100 kJ/mol) the degradation is really slow and the concentration of PCE remains the same during the whole modelled time interval.

Comparisons of numerical and analytical models show that the values of reaction rate constant calculated analytically by using Arrhenius equation for ATES system (Hartog, 2011) correspond to the higher temperature than gives the numerical model. This is because the temperature in aquifer is lower than the temperature used in the analytical solution, see the results of the heat transport models. To get more accurate results, it is necessary to use the numerical models rather than the analytical solution.

The results of models can be more exact, if a better knowledge of reaction rate constant for different temperatures is available. The applied values were obtained from different sources and consequently under different conditions.

Due to the limited sources, the results for zero order reactions are not so reliable in comparison with those of the first order. The zero order reaction rate constants had to be calculated by multiplication of the first order reaction rate constant and by reference concentration. The results of these models depend mostly on the value of chosen reference concentrations. Despite this, it was shown that the effect of temperature on concentration is more or less similar to the results of models with first order reactions.

However, ATES system does not affect biodegradation only by the changes in temperature. Change of oxidation-reduction conditions could affect the biodegradation rates of chlorinated hydrocarbons as well as their degradation products. The changes in oxidation-reduction conditions are caused by mixing of water from different depth with different oxidation-reduction conditions. Unlike the temperature, the oxidation-reduction conditions are very important for biodegradation of chlorinated hydrocarbons. In the future studies, it would be interesting to create a model containing more detailed information about the oxidation-reduction conditions on the locality site. It can be concluded that, under suitable conditions, ATES system could be used as one of the possible remediation methods of chlorinated hydrocarbons.

According to the heat transport models, the heat convection is very small and the changes in the temperature occur only around the wells as they are only due to advection. This also confirms the basic principle of the ATES system that the water stays only around the wells. Spreading into the aquifer is insignificant, and therefore, it allows for pumping and injecting the water of different temperature from and into the aquifer.

Besides the heating and cooling the buildings, the ATES system can also be used, in case of suitable oxidation-reduction conditions, as a remediation method for removing chlorinated hydrocarbons from the aquifer.

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